Supporting Information

Chiral Expression in Conjugated Helical Block Copolymers

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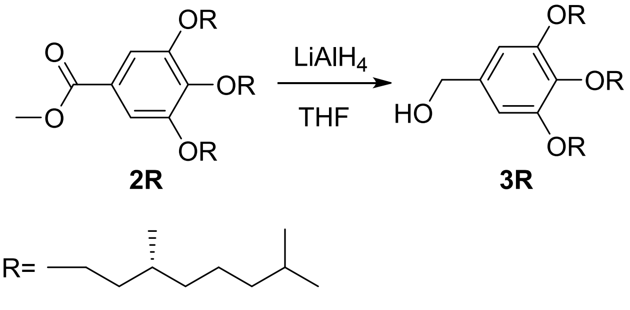
Contents

Experimental Information

All reagents were purchased from TCI, Sigma-Aldrich, J&K Scientific and Acros Organics and used without further purification. 2,2,6,6-Tetramethylpiperidinylmagnesium chloride lithium chloride complex was titrated before use according to the procedure by Love *et al.*[1] Reagent grade solvents were dried by a solvent purification system MBRAUN SPS 800 (columns with activated alumina). ^{1}H NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. ^{13}C-NMR-spectra were measured on a Bruker Avance 600 MHz-spectrometer. Size exclusion chromatography (SEC) measurements were carried out on a Shimadzu 20A GPC system. The column is a PLgel 5 μm mixed-D type column, and the detection system consists of a differential refractometer and a UV−vis spectrophotometer. The GPC system is calibrated toward polystyrene standards (purchased from Polymer Laboratories). Before measuring, the polymers are dissolved in THF (c ≈ 1 mg/mL) and filtered over a pore size of 0.2 μm. UV−vis measurements were performed on a Varian 400 Scan. CD-measurements were performed on a Jasco J-1500. Compounds **5**[2], **2R**[3], **4B**[4], **6S**[5] and **7**[6] were prepared according to literature procedures.

Synthesis of the monomers

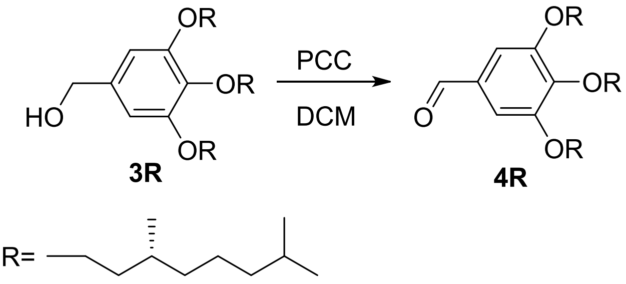
Synthesis of compound 3R.



2R (24.0 mmol, 14.6 g) was brought under N_2-atmosphere and dissolved in dry THF (100 ml). It was then added dropwise to an ice-cooled suspension of $LiAlH_4$ (38.4 mmol, 1.46 g) in

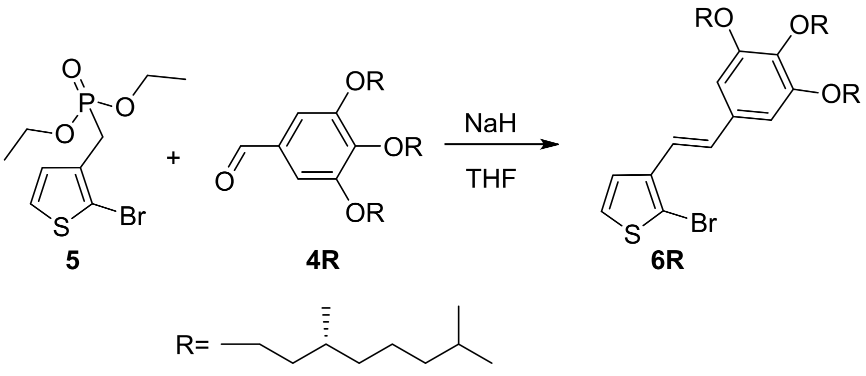
THF (16 ml). After complete addition, the ice bath was removed and the mixture was heated at reflux and monitored via TLC (SiO_2, DCM/EtOAc 8/2) until complete conversion (3 hours). The mixture is then cooled to 0°C and added to ice, after which a 2M HCl-solution is added. The product is extracted with diethyl ether and the combined organic layers are dried over $MgSO_4$. The solvent is removed under reduced pressure and the product is isolated as a yellowish oil. Yield: 11.7 g (84%) ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 6.58 (s, 2H), 4.61 (d, 2H, 6.0 Hz), 3.98 (m, 6H), 1.86 (m, 3H), 1.60 (m, 9H), 1.26 (m, 19H), 0.94 (d, 9H, 6.6 Hz), 0.87 (d, 18H, 6.6 Hz) ^{13}C-NMR (CDCl3, 150 MHz) δ (ppm) = 153.4, 137.6, 136.0, 105.3, 71.7, 67.4, 65.7, 39.4, 39.3, 37.5, 37.4, 36.4, 29.8, 29.7, 28.0, 24.7, 22.7, 22.6, 22.6, 19.6, 19.6 MS (ESI) (m/z): 575.4

Synthesis of compound 4R.



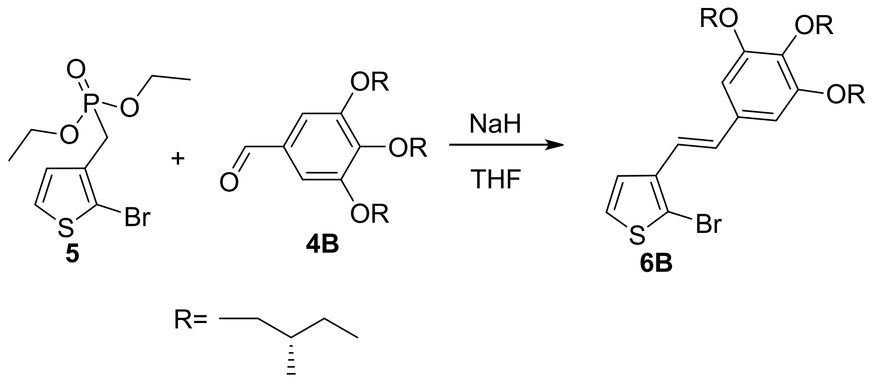
3R (20.3 mmol, 11.7g) was dissolved in dry DCM (80 ml) and added to pyridinium chlorochromate (PCC) (30.4 mmol, 6.55 g) in dry DCM (70 ml). The mixture was stirred at room temperature for 3 hours and filtered over silica using diethyl ether. The solvent was then removed under reduced pressure and the pure product was isolated as a yellow oil. Yield: 10.4g (89%) ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 9.84 (s, 1H), 7.08 (s, 2H), 4.10 (m, 6H), 1.86 (m, 3H), 1.59 (m, 9H), 1.24 (m, 18H), 0.94 (d, 9H, 6.6 Hz), 0.87 (d, 18H, 6.6 Hz) ^{13}C-NMR (CDCl3, 150 MHz) δ (ppm) = 191.4, 153.5, 143.8, 131.5, 107.8, 71.9, 67.6, 39.3, 39.2, 37.5, 37.3, 36.3, 29.9, 29.6, 28.0, 24.7, 22.7, 22.6, 19.6, 19.5 MS (ESI) (m/z): 575.4

Synthesis of compound 6R.



Under N_2-atmosphere, NaH (5.30 mmol, 0.13 g) was suspended in dry THF (10 ml). **4R** (5.30 mmol, 3.02 g) in dry THF (5 ml) and **5** (4.80 mmol, 1.50 g) in THF (5 ml) were added respectively. The reaction mixture was heated until reflux and the reaction was monitored with TLC (SiO_2, heptane/DCM 7/3). After complete conversion, the reaction mixture was added to water and a 1M HCl-solution was added. The product was extracted with DCM and the combined organic layers were washed with a $NaHCO_3$ and NaCl solution respectively. The organic layer was dried using $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified via column chromatography (SiO_2, heptane/DCM 7/3) and isolated as a yellowish oil. Yield: 1.23 g (35%) ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 7.25 (d, 1H, 5.9 Hz), 7.19 (d, 1H, 5.9 Hz), 6.96 (d, 1H, 16Hz), 6.88 (d, 1H, 16Hz), 6.71 (s, 2H), 4.02 (m, 6H), 1.87 (m, 3H), 1.59 (m, 9H), 1.25 (m, 18H), 0.95 (d, 9H, 6.6 Hz), 0.87 (d, 18H, 6.6 Hz) ^{13}C-NMR (CDCl3, 150 MHz) δ (ppm) = 153.4, 138.6, 138.2, 132.2, 130.9, 126.0, 124.6, 120.1, 110.9, 105.3, 71.8, 67.5, 39.4, 39.3, 37.5, 37.4, 37.4, 36.5, 29.8, 29.7, 28.0, 24.8, 24.7, 22.7, 22.6, 19.6, 19.6 MS (ESI) (m/z): 734.4

Synthesis of compound 6B.



The same procedure as described for **6R** was followed, using **4B** (3.80 mmol, 1.38 g) instead of **4R**. Yield: 0.82 g (46%) 1H-NMR (CDCl3, 300 MHz) δ (ppm) = 7.25 (d, 1H, 5.9 Hz), 7.18 (d, 1H, 5.9 Hz), 6.96 (d, 1H, 16 Hz), 6.88 (d, 1H, 16 Hz), 6.69 (s, 2H), 3.82 (m, 6H), 1.87 (m, 3H), 1.62 (m, 3H), 1.29 (m, 3H), 1.05 (d, 9H, 6.6 Hz), 0.96 (t, 9H, 7.4 Hz) 13C-NMR (CDCl3, 150 MHz) δ (ppm) = 153.5, 138.5, 138.3, 132.2, 131.0, 126.0, 124.7, 120.0, 110.8, 104.9, 78.7, 73.9, 35.8, 34.9, 26.2, 16.7, 11.4, 11.4 MS (ESI) (m/z): 525.1

Synthesis of the polymers

Synthesis of the block copolymers made from enantiomers **1** and **2**

The reagent quantities and reaction yields can be found in Table S 1. The quantities for the initiator are found in Table S 2.

Two flasks were charged with respectively **6S** and **6R** and purged with N_2. 2,2,6,6-tetramethylpiperidinylmagnesium chloride (TMPMgCl.LiCl) was added and the resulting mixture was stirred for three hours at room temperature. Compound **7** and 1,3-bis(diphenylphosphino)propane were added to a flask and brought under N_2-atmosphere. THF (1 ml) was added and the mixture is stirred at room temperature for 15 minutes to obtain initiator **8**. After three hours, the flasks containing **6S** and **6R** were diluted with dry THF until a monomer concentration of 0.1M. The first monomer was then cannulated into the initiator flask. After 10 minutes of polymerization time, a small quantity of polymer was taken out and terminated by addition of 2M HCl in THF for GPC-analysis. The second monomer was then added. After 35 minutes, the polymerization was terminated using a 2M HCl in THF solution. The polymer was then precipitated in methanol and purified via Soxhlet extraction using methanol and chloroform. The chloroform layer was concentrated under reduced pressure and again precipitated in methanol. The polymer was filtered on a glass sintered filter and dried under vacuum. It was isolated as a red powder.

*Table S 1. Reagent quantities and yields for the monomer synthesis for polymers **P1**-**P6***

	Compound **6S**			Compound **6R**			
	Amount (mmol)	Mass (mg)	TMPMgCl.LiCl (0.81M) (ml)	Amount (mmol)	Mass (mg)	TMPMgCl.LiCl (0.81M) (ml)	Yield (mg/%)
P1	0.30	220	0.35	0	0	0	117/59%
P2	0.26	190	0.30	0.04	30	0.05	102/62%
P3	0.22	160	0.25	0.08	61	0.09	110/67%
P4	0.15	110	0.19	0.05	37	0.06	50/51%
P5	0.18	128	0.20	0.13	92	0.15	107/66%
P6	0.13	91	0.15	0.08	55	0.09	65/66%

*Table S 2. Reagent quantities for the initiator synthesis for polymers **P1**-**P6***

	7		dppp	
	Amount (µmol)	Mass (mg)	Amount (µmol)	Mass (mg)
P1, **P2**, **P3**, **P5**	8.3	7.13	16.6	6.87
P4, **P6**	5	4.28	10	4.12

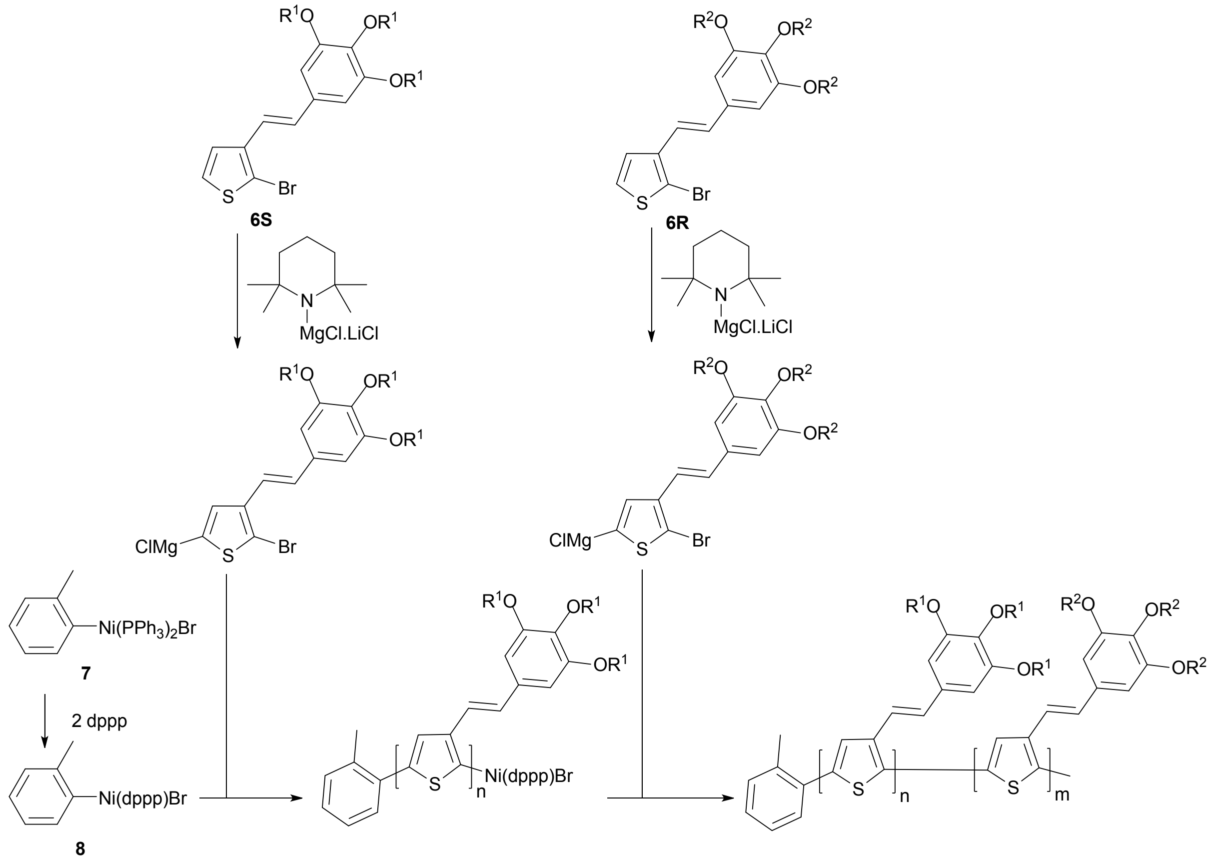


*Figure S 1. Scheme for the synthesis of block copolymers **P1**-**P6***

Synthesis of the block copolymers made from **3** and **1**

For these polymers, the same procedure as for the first series of block copolymers was used with **6B** instead of **6S** and **6S** instead of **6R**. The used quantities and reaction yields can be found in Tables S3 and S4.

*Table S 3. Reagent quantities and yields for the monomer synthesis for polymers **P7**-**P14***

	Compound **6B**			Compound **6S**			
	Amount (mmol)	Mass (mg)	TMPMgCl.LiCl (0.81M) (ml)	Amount (mmol)	Mass (mg)	TMPMgCl.LiCl (0.81M) (ml)	Yield (mg/%)
P7	0.15	78	0.19	0	0	0	36/55%
P8	0.19	97	0.23	0.02	11	0.02	30/48%
P9	0.18	92	0.21	0.03	18	0.03	50/66%
P10	0.15	78	0.19	0.05	36	0.06	30/38%
P11	0.08	65	0.15	0.08	55	0.09	48/59%
P12	0.05	26	0.06	0.12	88	0.15	38/38%
P13	0.09	46	0.11	0.11	82	0.14	65/66%
P14	0.10	52	0.12	0.22	161	0.27	75/40%

*Table S 4. Reagent quantities for the initiator synthesis for polymers **P7**-**P14***

	7	dppp

	Amount (µmol)	Mass (mg)	Amount (µmol)	Mass (mg)
P7	6	5.13	12	4.95
P8, **P9**, **P10**, **P11**	5	4.28	10	4.12
P12	11	8.2	22	9.2
P13	12	10.0	24	9.7
P14	17	14.2	33	13.7

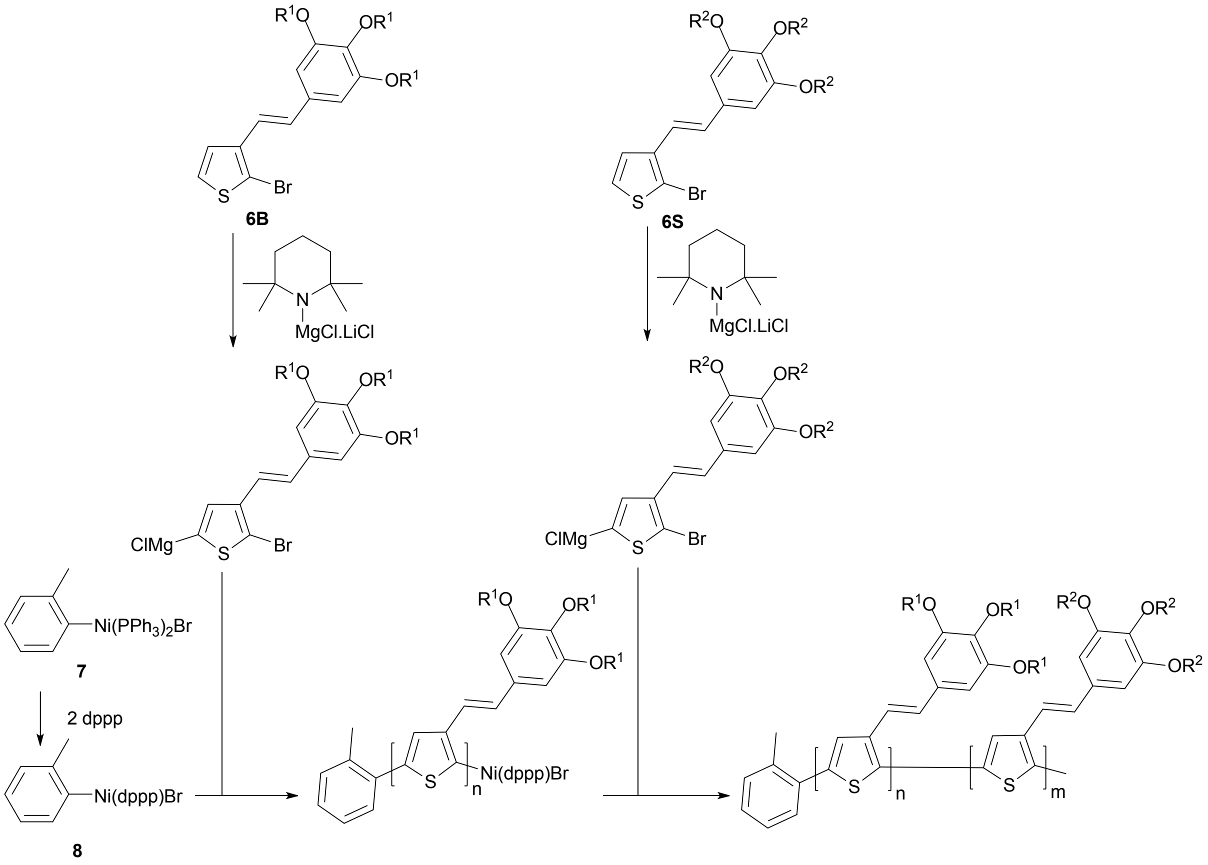


*Figure S 2. Scheme for the synthesis of block copolymers **P7**-**P12***

GPC-Chromatograms

GPC chromatograms were measured for both blocks of all block copolymers. The GPC of the first block is in black, GPC after addition of the second block in red. For homopolymers **P1** and **P7** only one chromatogram was measured as there was only one monomer addition. The peak at 10.5 min belongs to BHT used to stabilise THF.

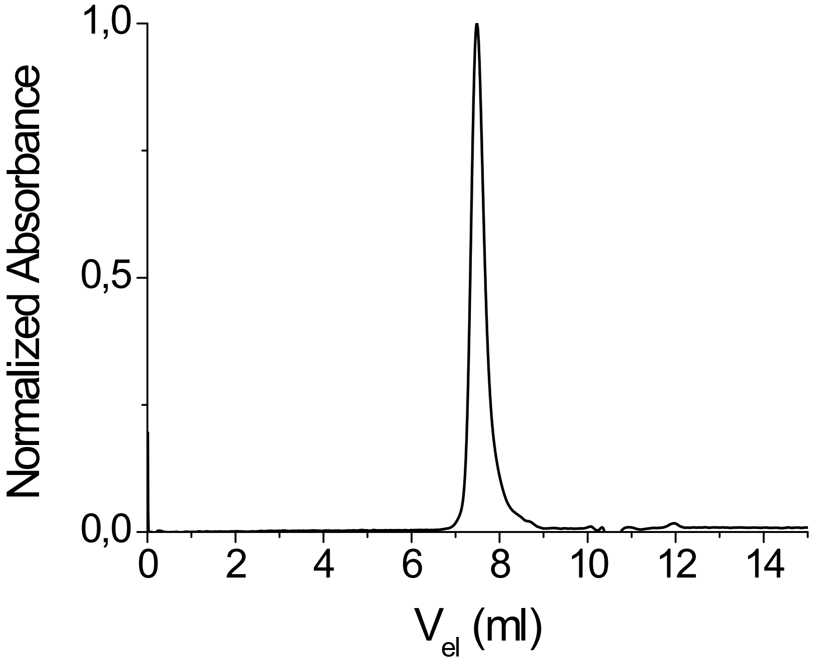


*Figure S 3. GPC-chromatogram of **P1***

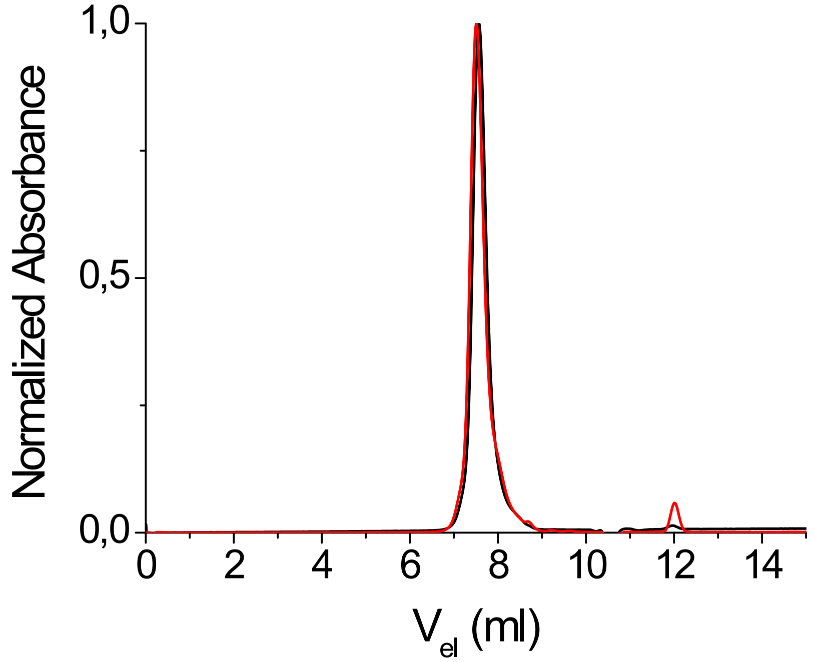


*Figure S 4. GPC-chromatogram of **P2**, first block is in black, the second in red*

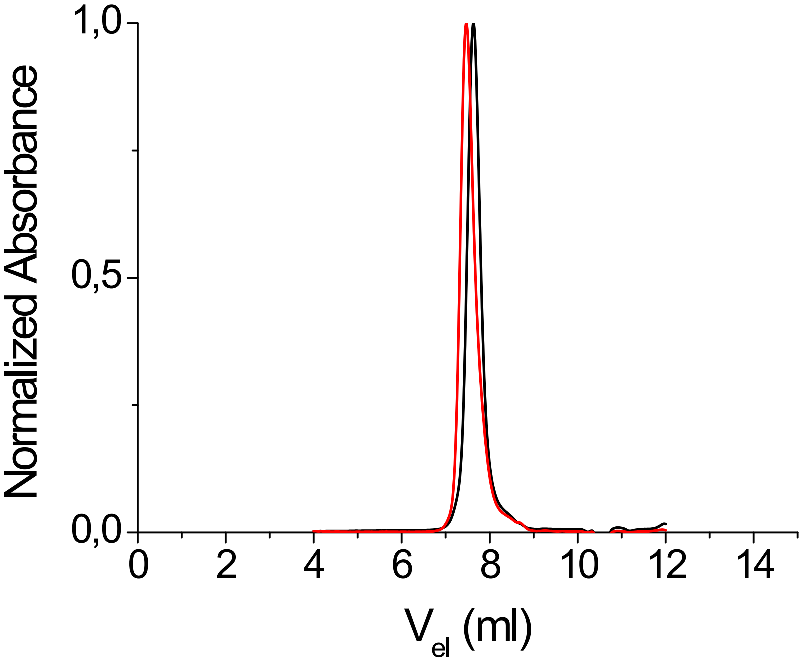


Figure S 5. GPC-chromatogram of ***P3****, first block is in black, the second in red*

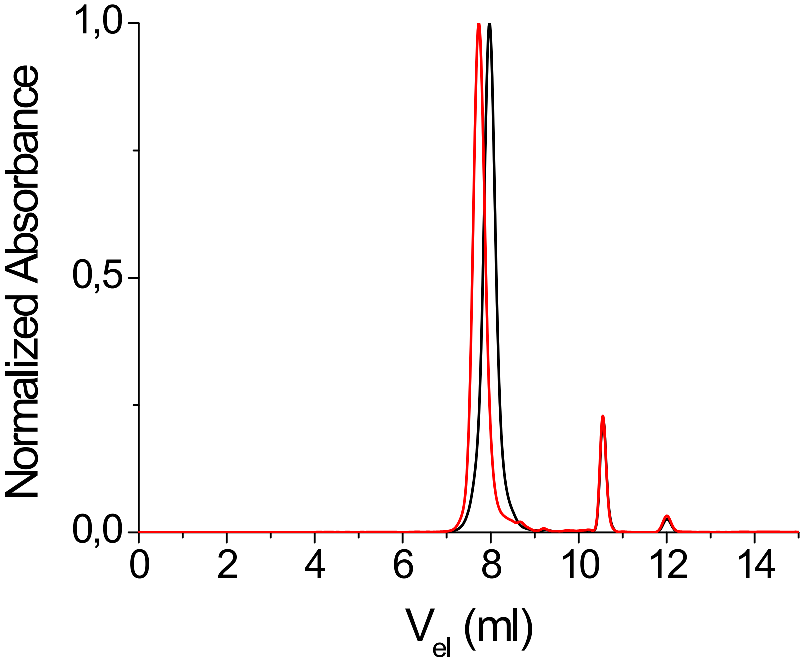


Figure S 6. GPC-chromatogram of ***P4****, first block is in black, the second in red*

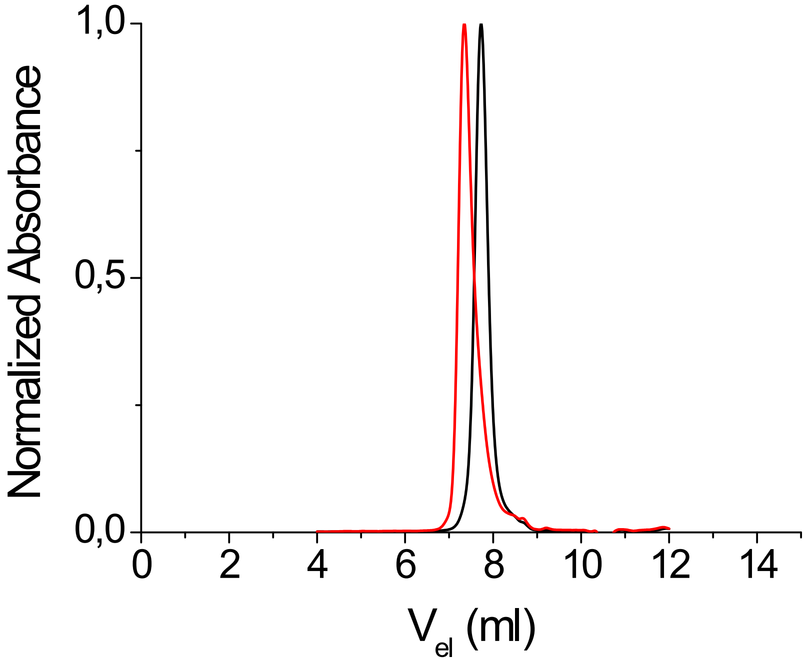


*Figure S 7. GPC-chromatogram of **P5**, first block is in black, the second in red*

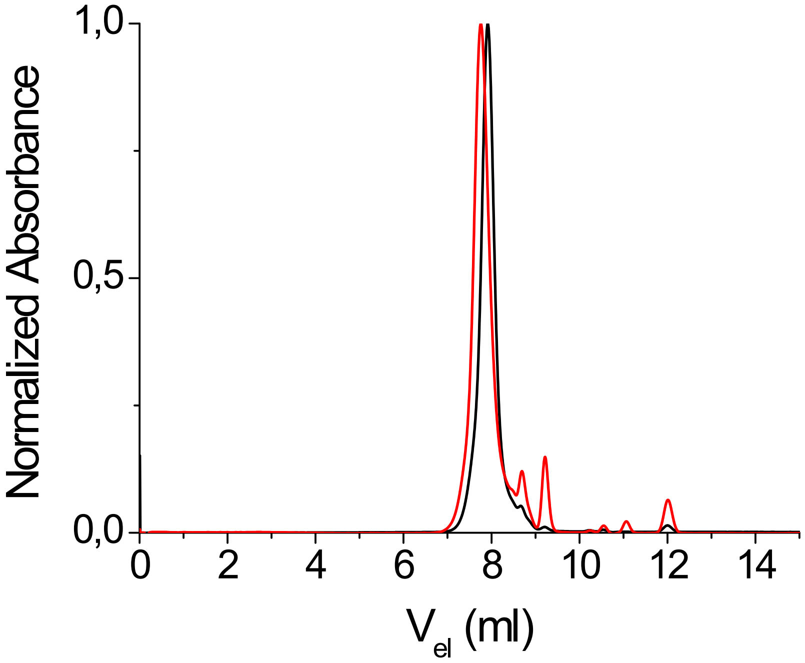


*Figure S 8. GPC-chromatogram of **P6**, first block is in black, the second in red*

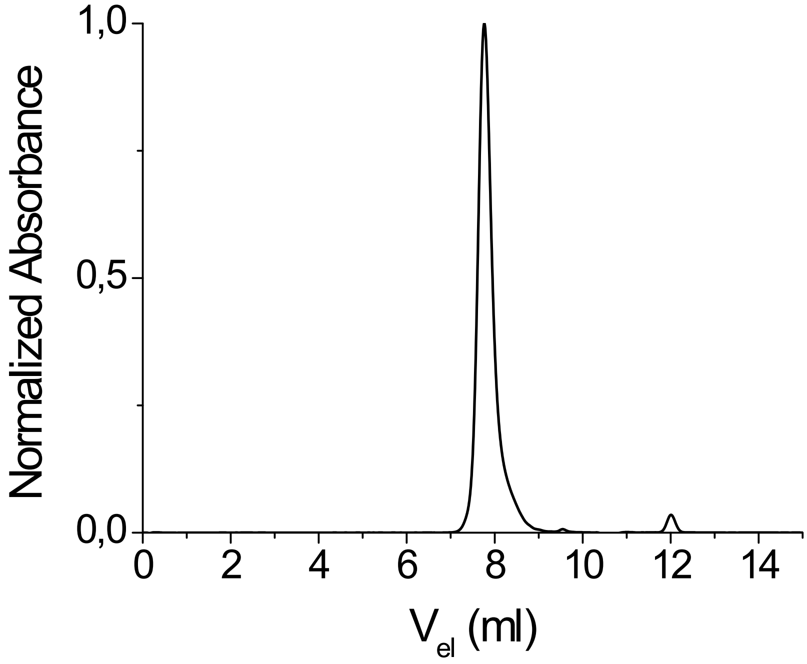


*Figure S 9. GPC-chromatogram of **P7***

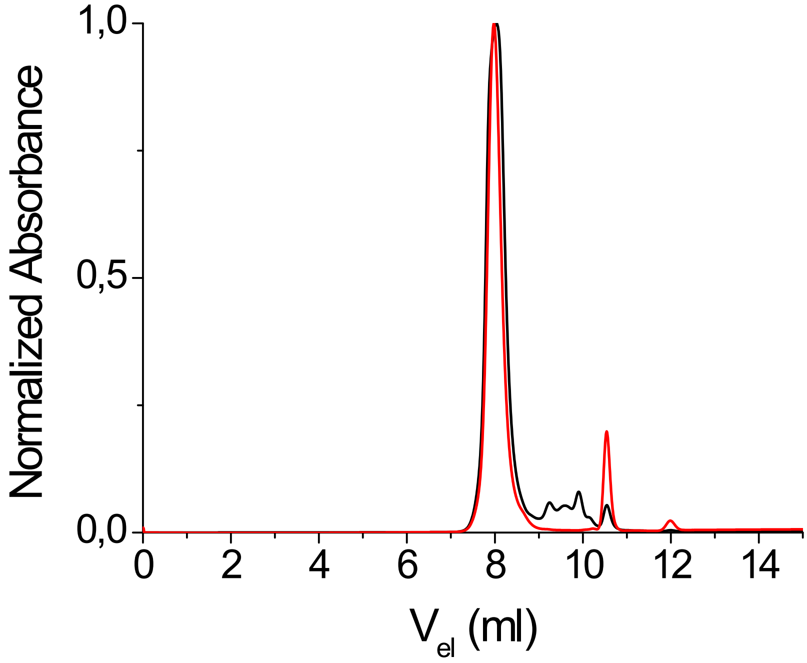


*Figure S 10. GPC-chromatogram of **P8**, first block is in black, the second in red*

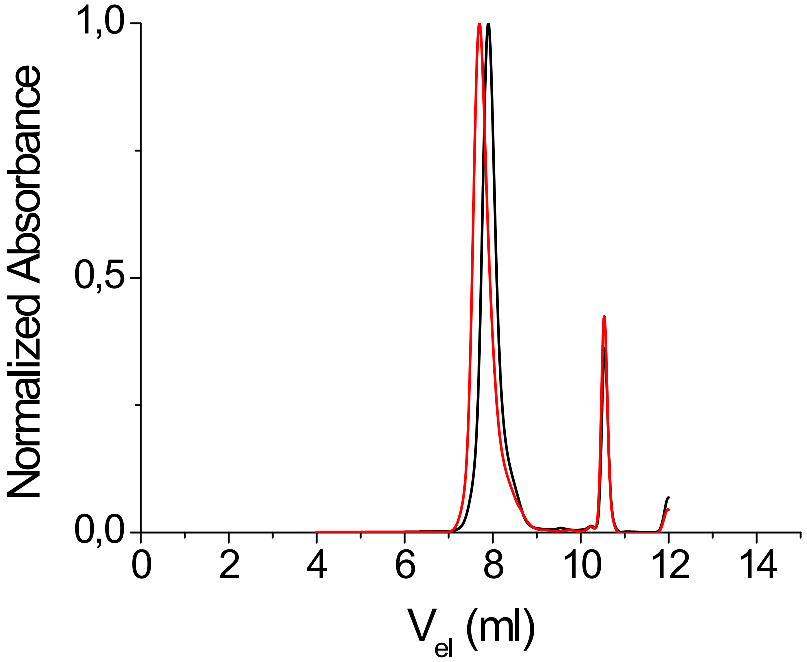


*Figure S 11. GPC-chromatogram of **P9**, first block is in black, the second in red*

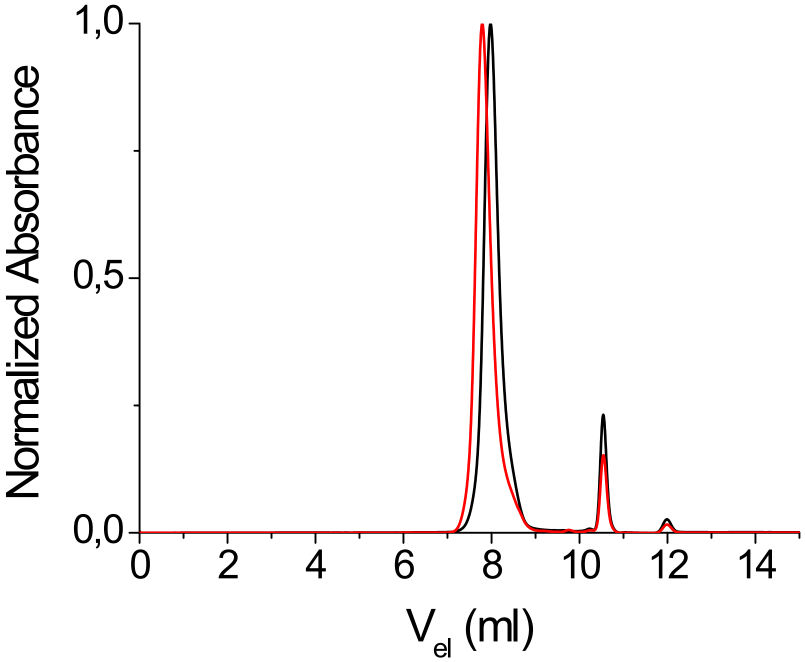


*Figure S 12. GPC-chromatogram of **P10**, first block is in black, the second in red*

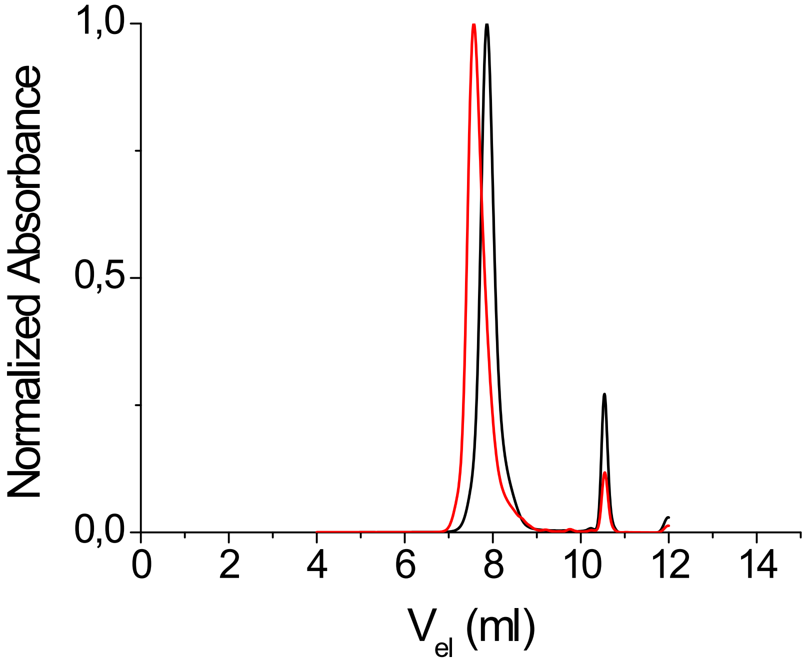


*Figure S 13. GPC-chromatogram of **P11**, first block is in black, the second in red*

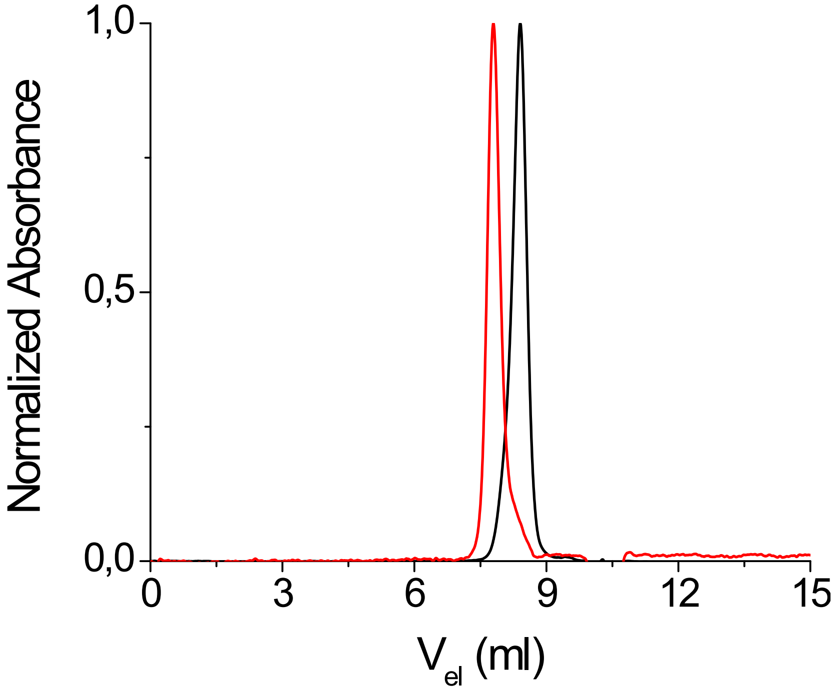


*Figure S 14. GPC-chromatogram of **P12**, first block is in black, the second in red*

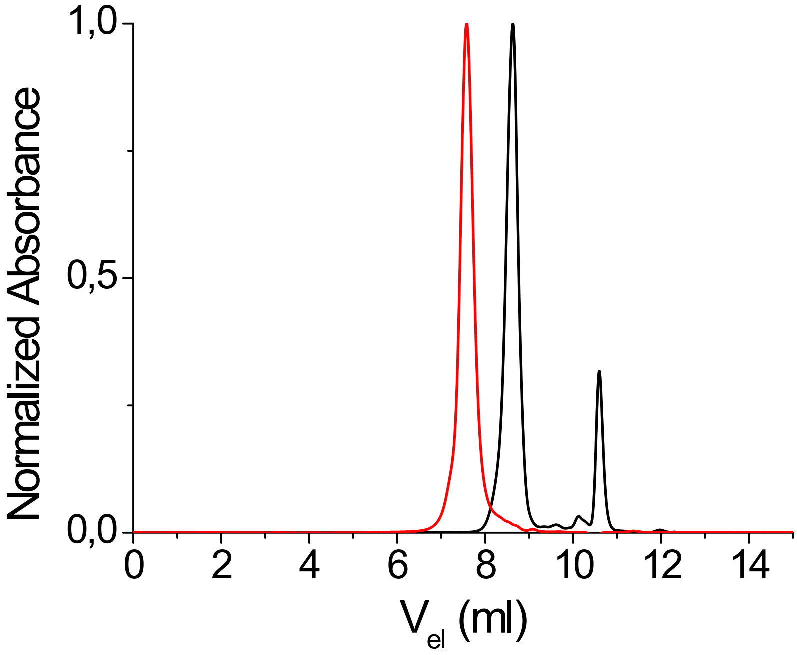


*Figure S 15. GPC-chromatogram of **P13**, first block is in black, the second in red*

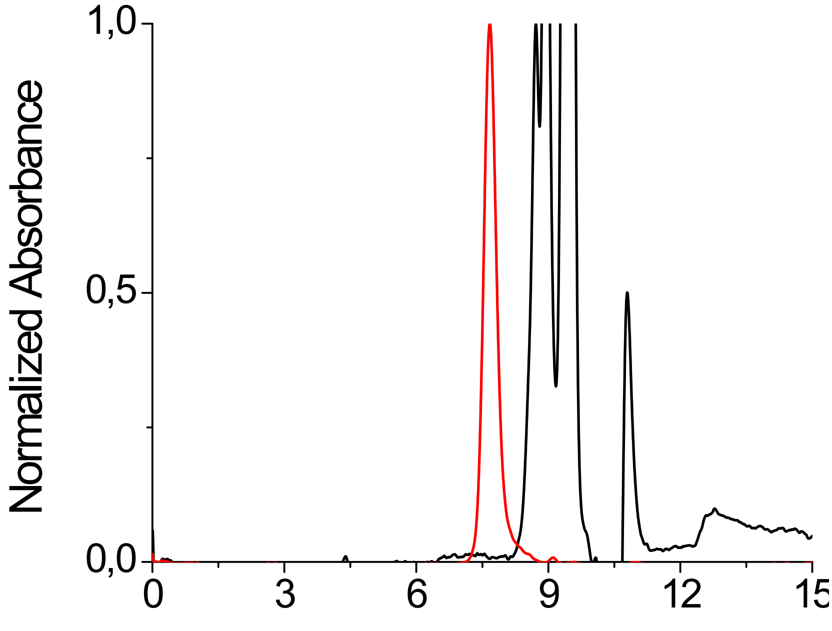


*Figure S 16. GPC-chromatogram of **P14**, first block is in black, the second in red. The chromatogram of the first block still contains monomer and stabilizer as purification via Soxhlet extraction was not possible due to the solubility of the short first block in methanol.*

UV-Vis and CD-spectra

The polymers were dissolved in chloroform and methanol was added at constant rate via a syringe pump. For the calculation of the standard deviation of the CD signal, the CD spectrum at the ratio $CHCl_3$/MeOH with highest CD intensity was recorded 5 times.

P1

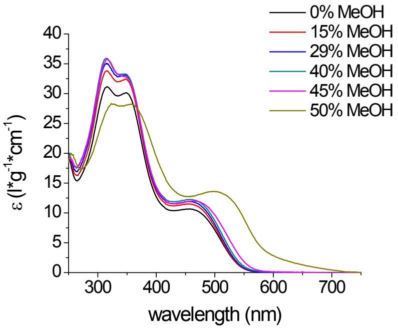


Figure S 17. Solvatochromism experiment for ***P1***

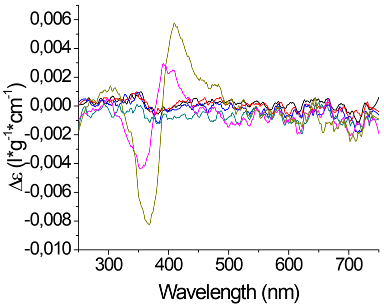


Figure S 18. CD-spectra at different ratios of $CHCl_3$ and methanol

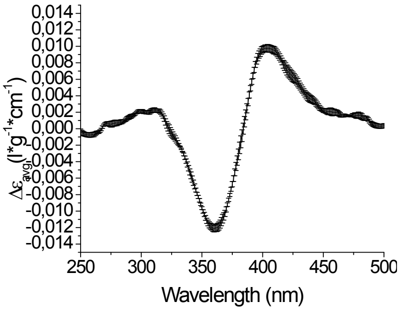


Figure S 19. Averaged CD spectrum of 5 measurements at 50% methanol

P2

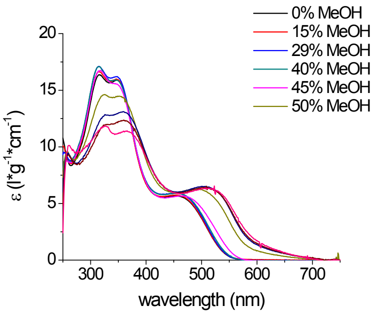


Figure S 20. Solvatochromism experiment for ***P2***

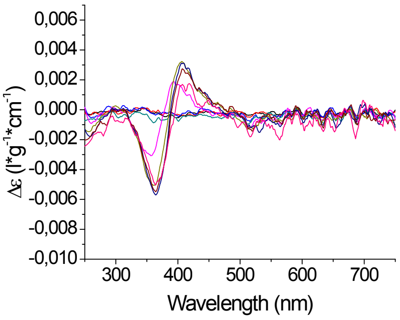


Figure S 21. CD-spectra at different ratios of $CHCl_3$ and methanol

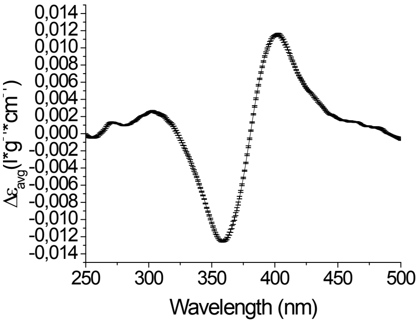


Figure S 22. Averaged CD spectrum of 5 measurements at 55% methanol

P3

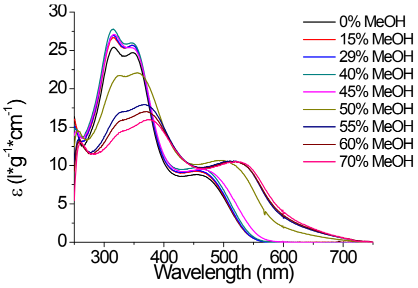


Figure S 23. Solvatochromism experiment for ***P3***

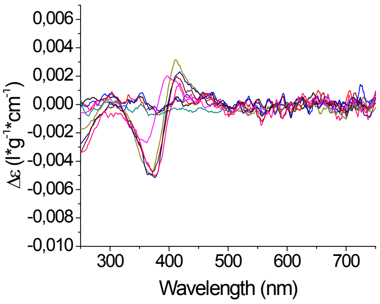


Figure S 24. CD-spectra at different ratios of $CHCl_3$ and methanol

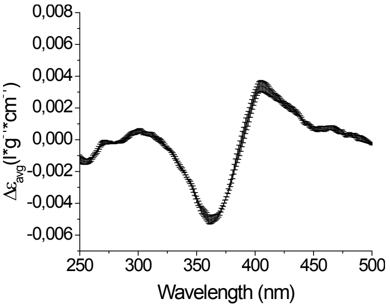


Figure S 25. Averaged CD spectrum of 5 measurements at 50% methanol

P4

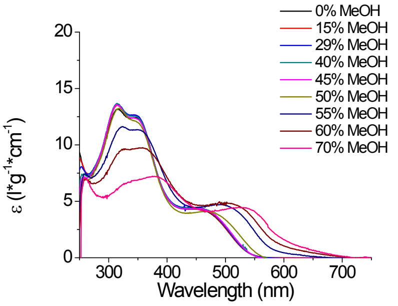


Figure S 26. Solvatochromism experiment for ***P4***

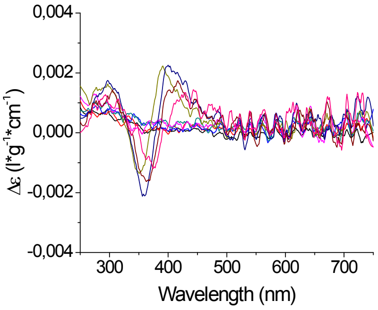


Figure S 27. CD-spectra at different ratios of $CHCl_3$ and methanol

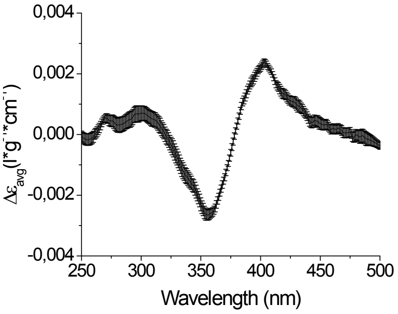


Figure S 28. Averaged CD spectrum of 5 measurements at 55% methanol

P5

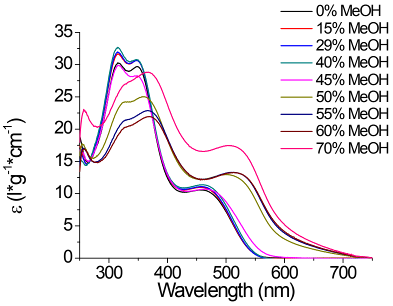


Figure S 29. Solvatochromism experiment for ***P5***

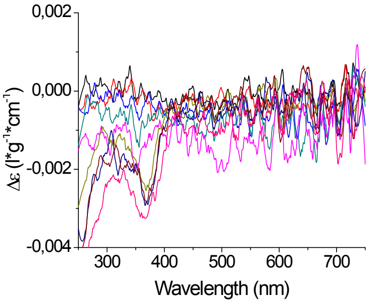


Figure S 30. CD-spectra at different ratios of $CHCl_3$ and methanol

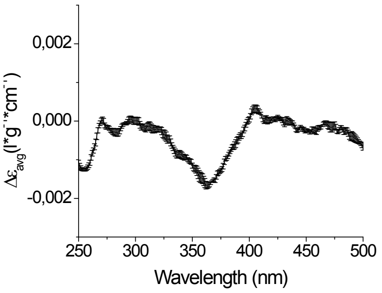


Figure S 31. Averaged CD spectrum of 5 measurements at 50% methanol

P6

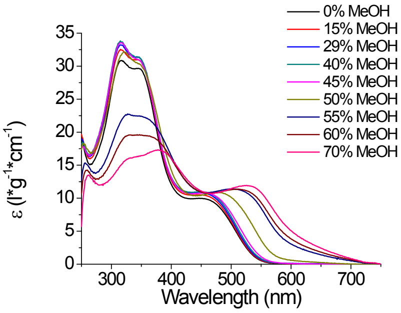


Figure S 32. Solvatochromism experiment for ***P6***

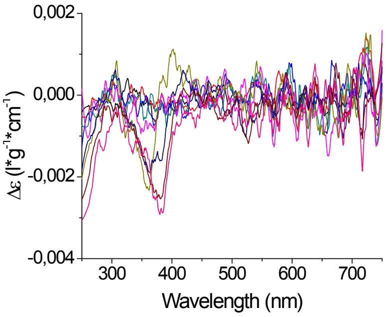


Figure S 33. CD-spectra at different ratios of $CHCl_3$ and methanol

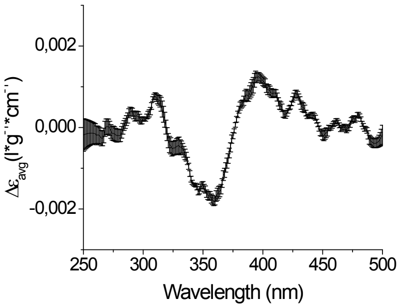


Figure S 34. Averaged CD spectrum of 5 measurements at 50% methanol

P7

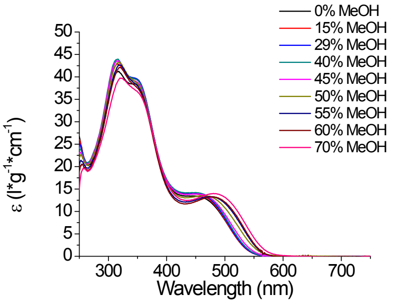


Figure S 35. Solvatochromism experiment for ***P7***

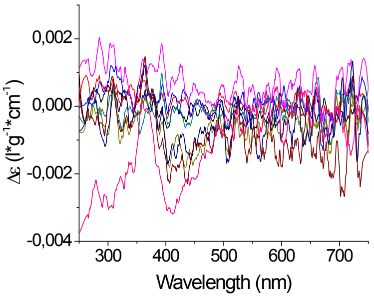


Figure S 36. CD-spectra at different ratios of $CHCl_3$ and methanol

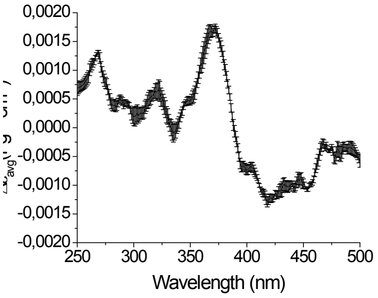


Figure S 37. Averaged CD spectrum of 5 measurements at 60% methanol

P8

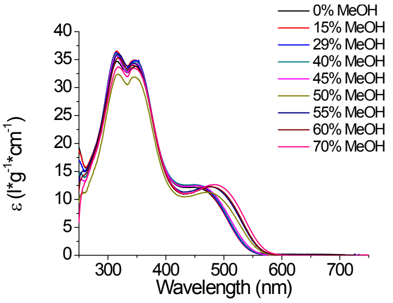


Figure S 38. Solvatochromism experiment for ***P8***

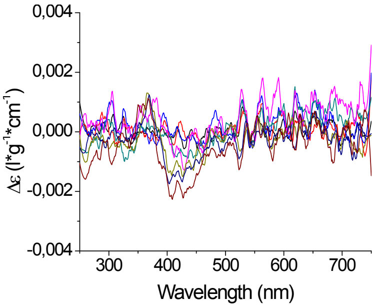


Figure S 39. CD-spectra at different ratios of $CHCl_3$ and methanol

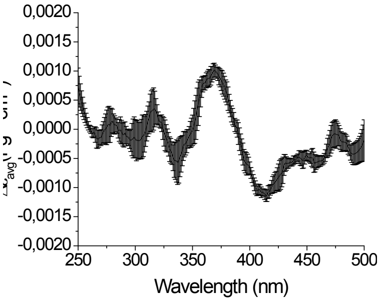


Figure S 40. Averaged CD spectrum of 5 measurements at 55% methanol

P9

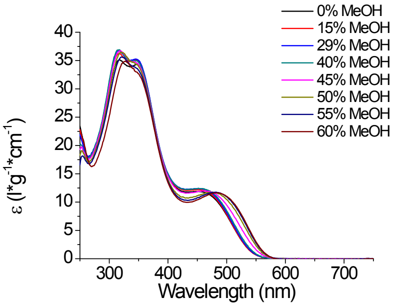


*Figure S 41. Solvatochromism experiment for **P9***

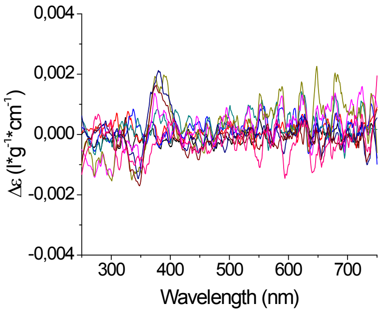


Figure S 42. CD-spectra at different ratios of $CHCl_3$ and methanol

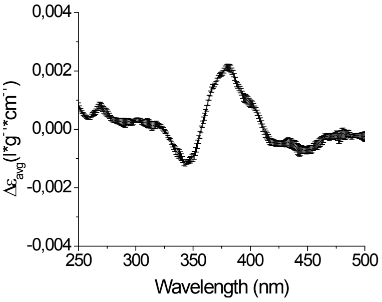


Figure S 43. Averaged CD spectrum of 5 measurements at 55% methanol

P10

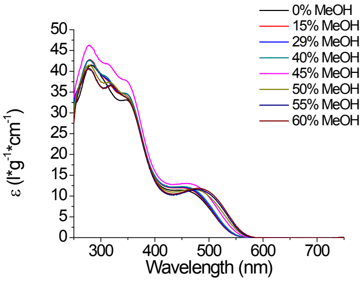


*Figure S 44. Solvatochromism experiment for **P10***

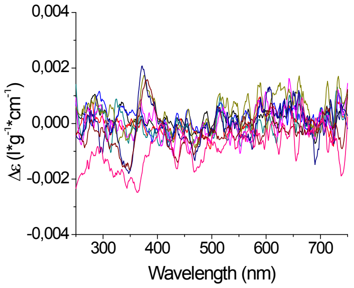


Figure S 45. CD-spectra at different ratios of $CHCl_3$ and methanol

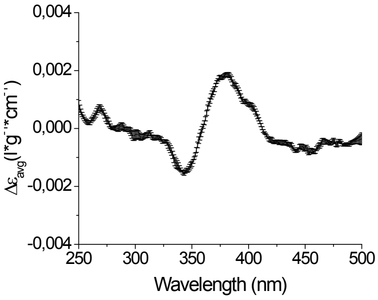


Figure S 46. Averaged CD spectrum of 5 measurements at 60% methanol

P11

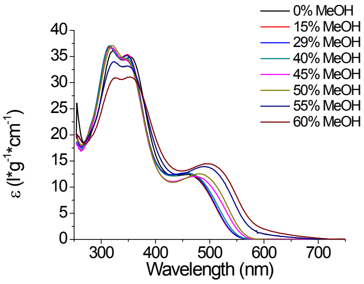


*Figure S 47. Solvatochromism experiment for **P11***

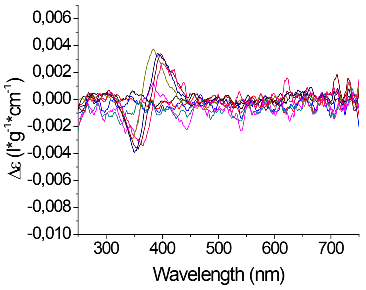


Figure S 48. CD-spectra at different ratios of $CHCl_3$ and methanol

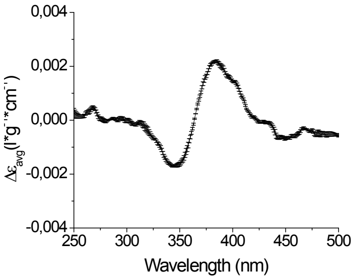


Figure S 49. Averaged CD spectrum of 5 measurements at 50% methanol

P12

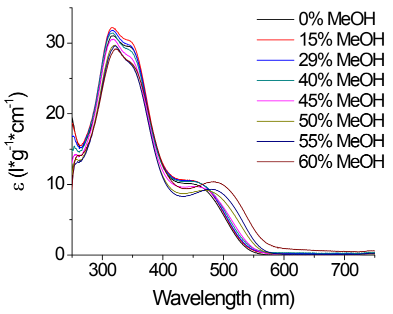


*Figure S 50. Solvatochromism experiment for **P12***

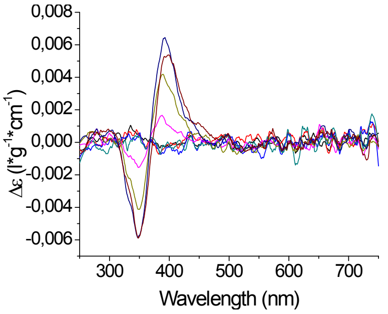


Figure S 51. CD-spectra at different ratios of $CHCl_3$ and methanol

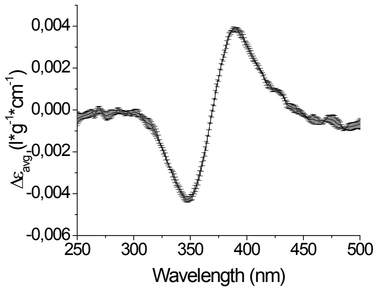


Figure S 52. Averaged CD spectrum of 5 measurements at 50% methanol

P13

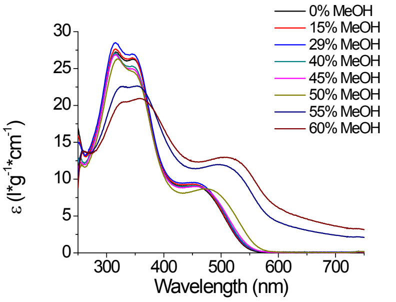


Figure S 53. Solvatochromism experiment for ***P13***

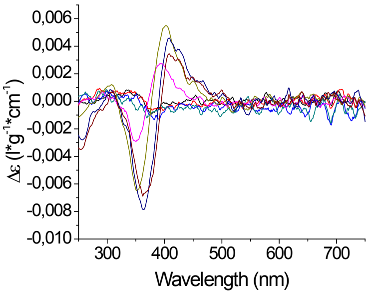


Figure S 54. CD-spectra at different ratios of $CHCl_3$ and methanol

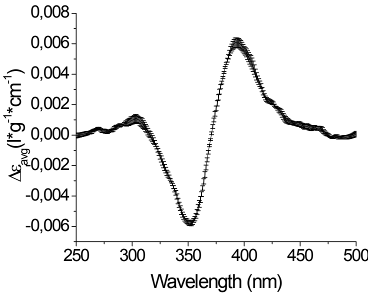


Figure S 55. Averaged CD spectrum of 5 measurements at 50% methanol

P14

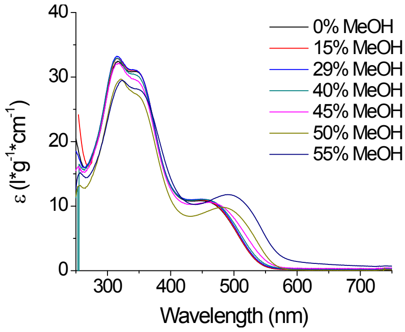


Figure S 56. Solvatochromism experiment for ***P14***

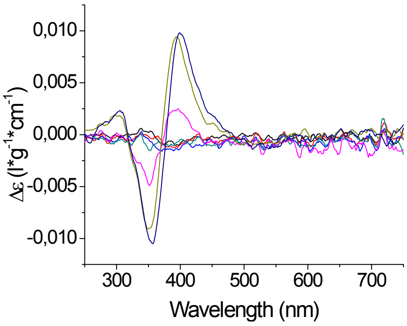


Figure S 57. CD-spectra at different ratios of $CHCl_3$ and methanol

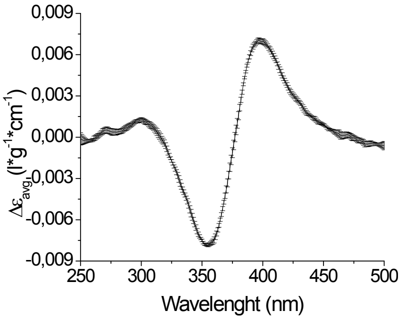


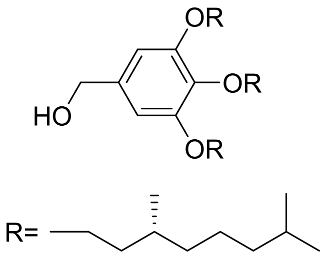
Figure S 58. Averaged CD spectrum of 5 measurements at 50% methanol

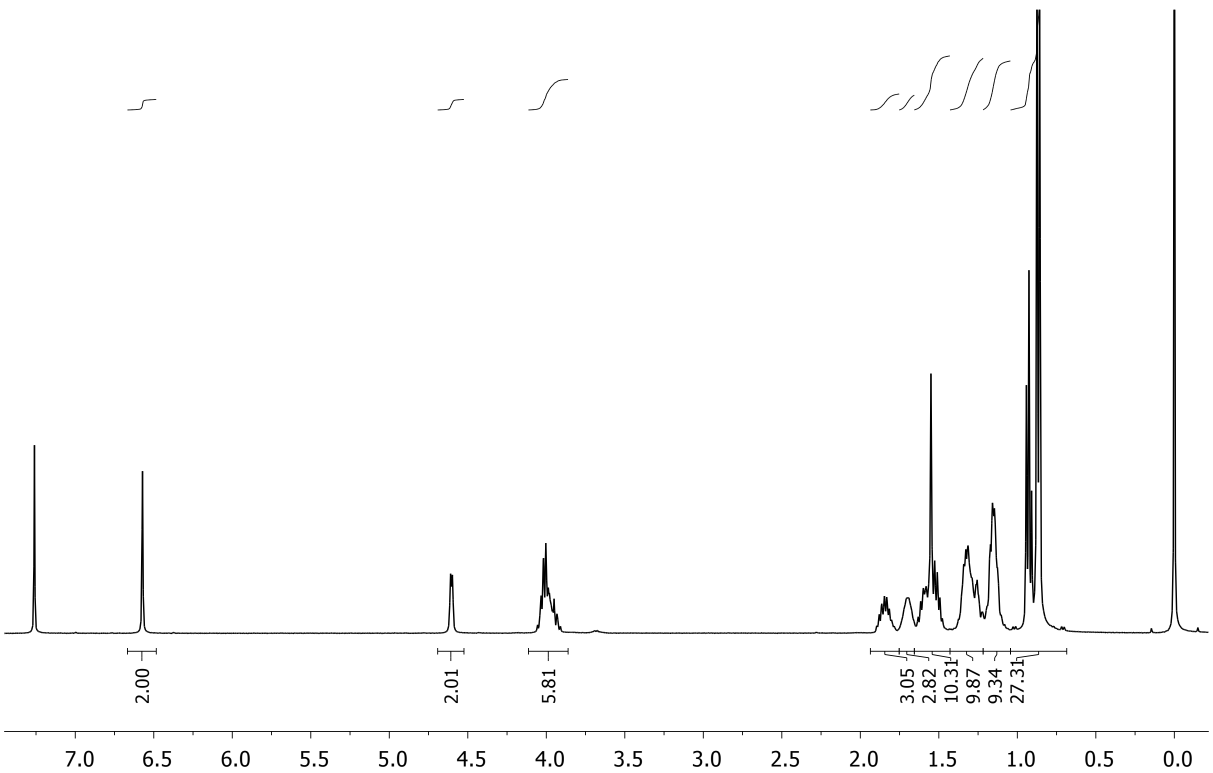
NMR spectra

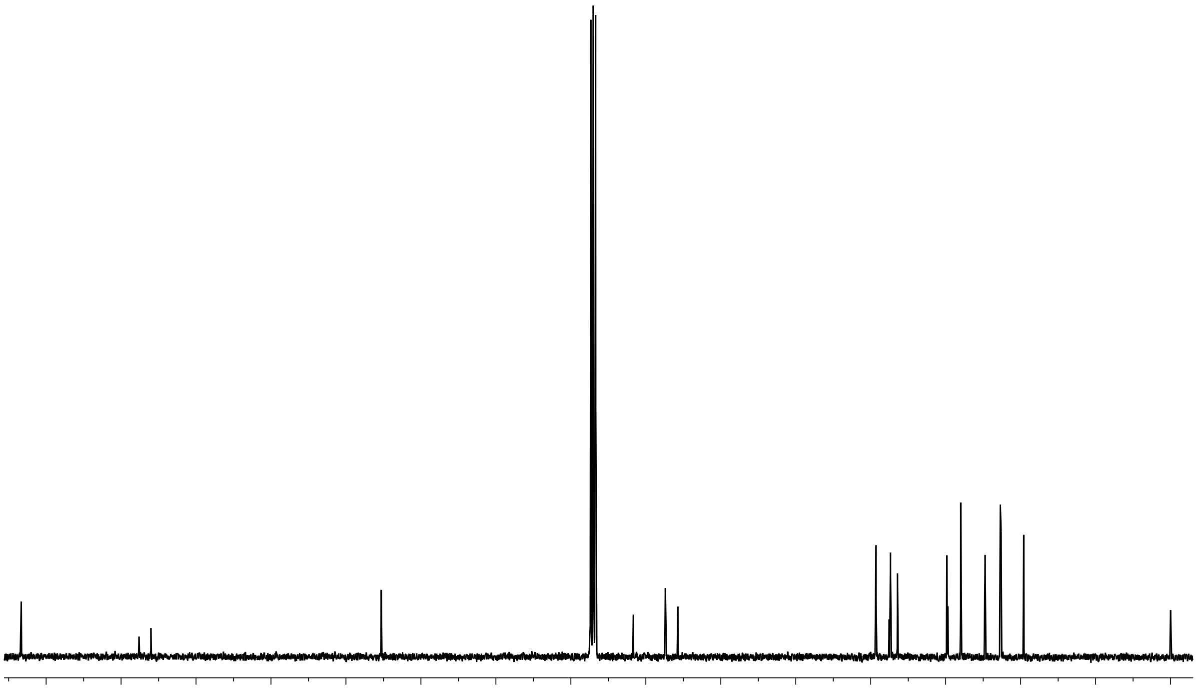
All spectra were recorded in $CDCl_3$ with 0.1 v/v TMS.

^1H NMR and ^{13}C NMR of the synthesized compounds

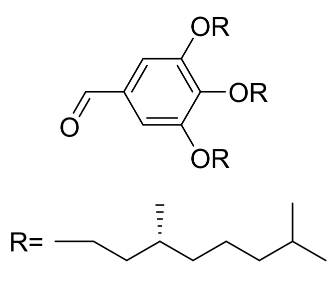
3R

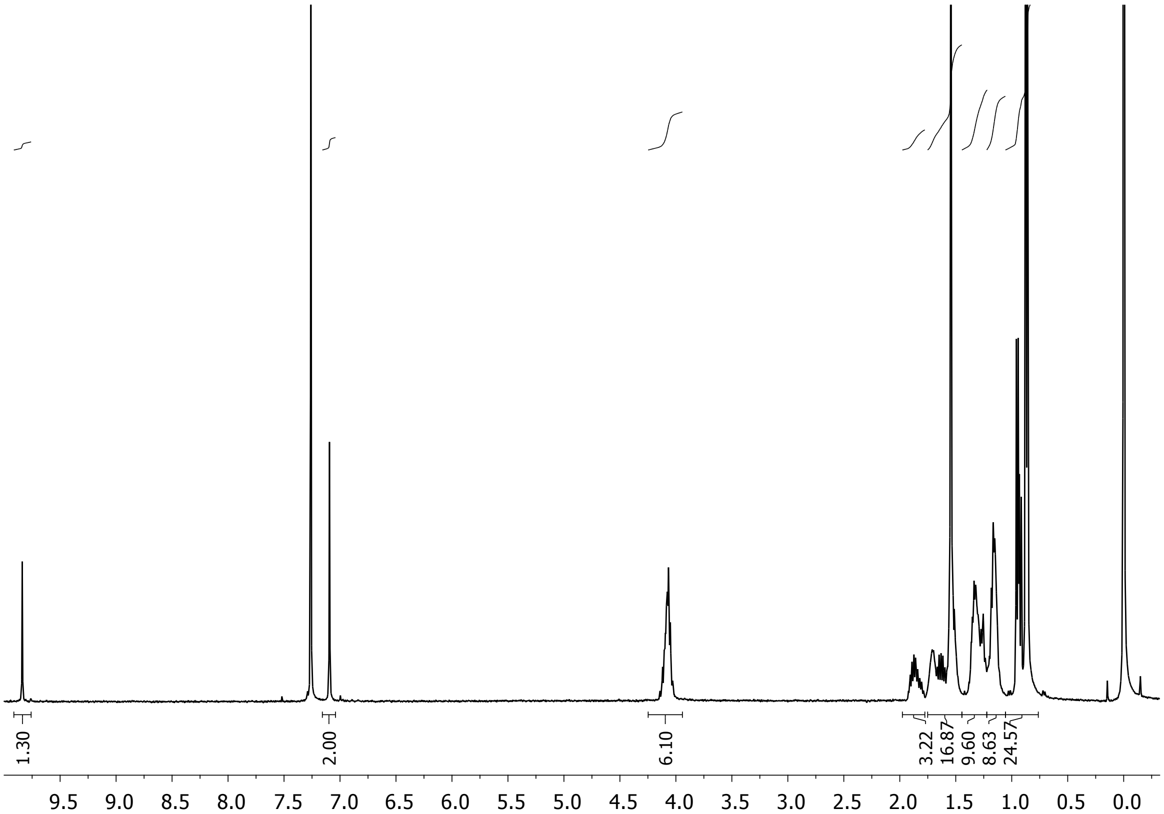


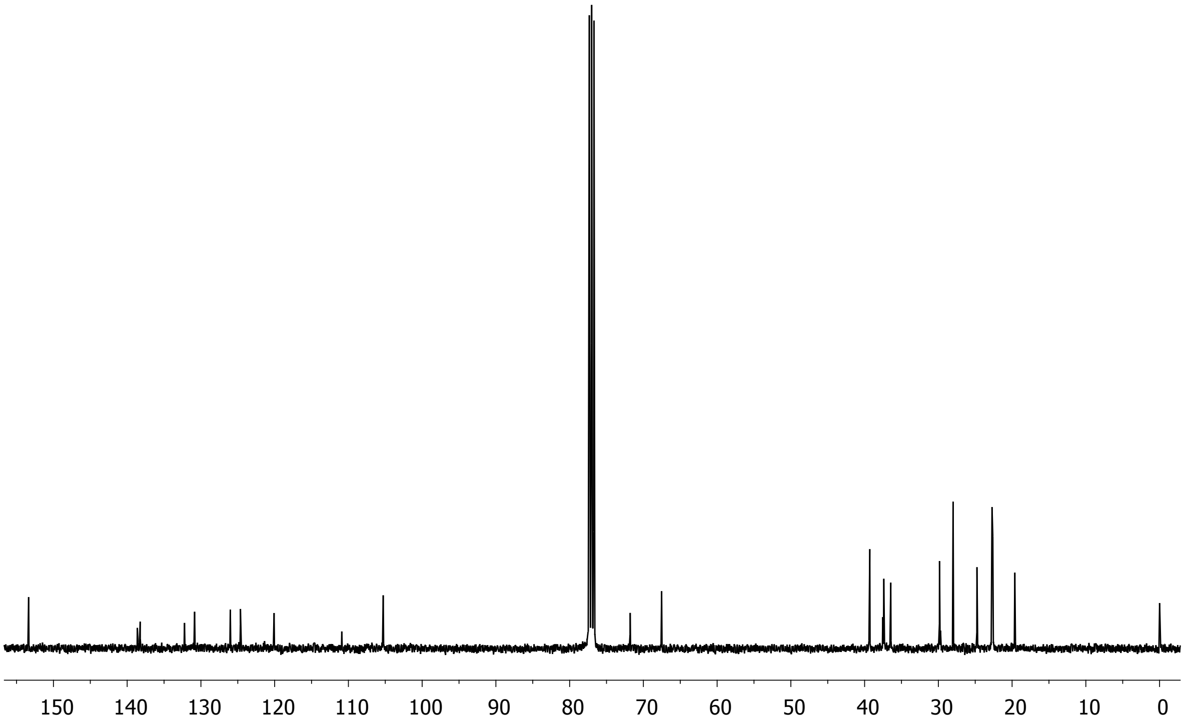

2.00
2.01
5.81
3.05
2.82
10.31
9.87
9.34
27.31
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

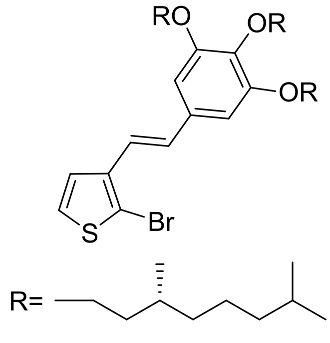
4R


OR
OR
OR
O
R=

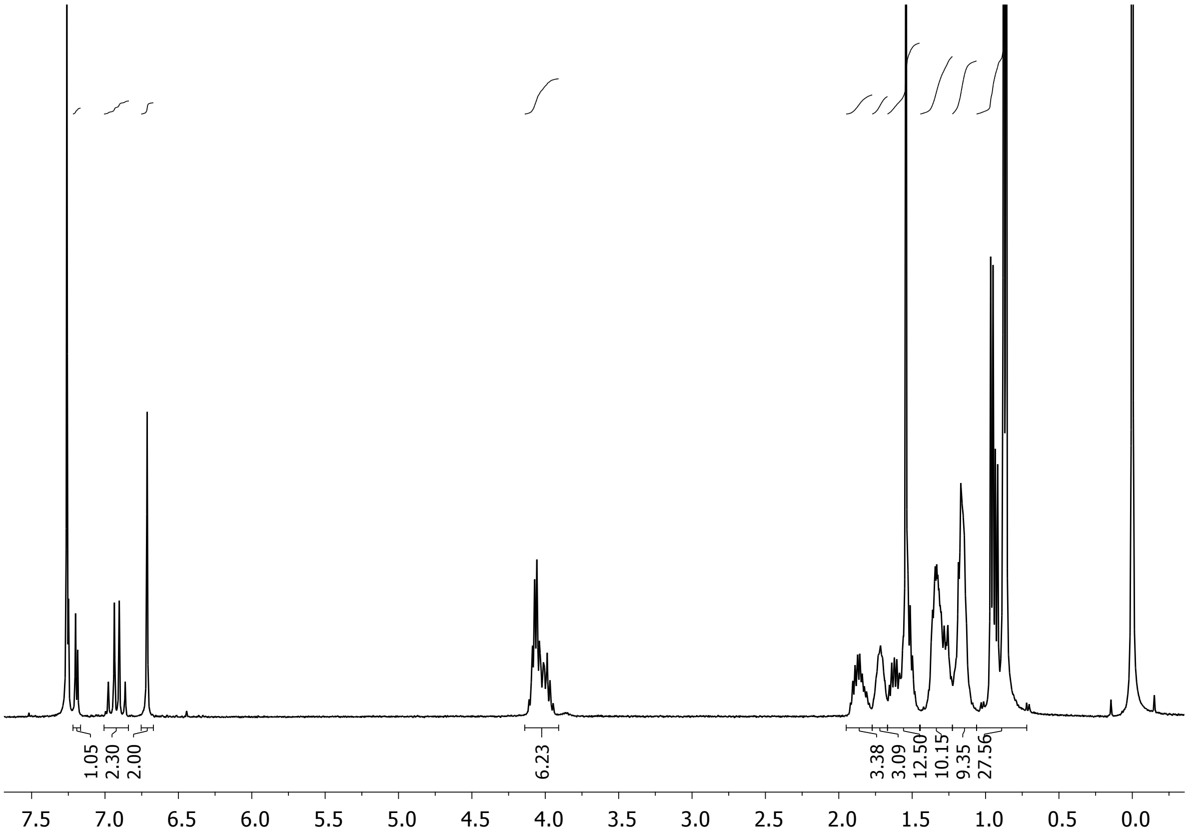

1.30
2.00
6.10
3.22
16.87
9.60
8.63
24.57
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

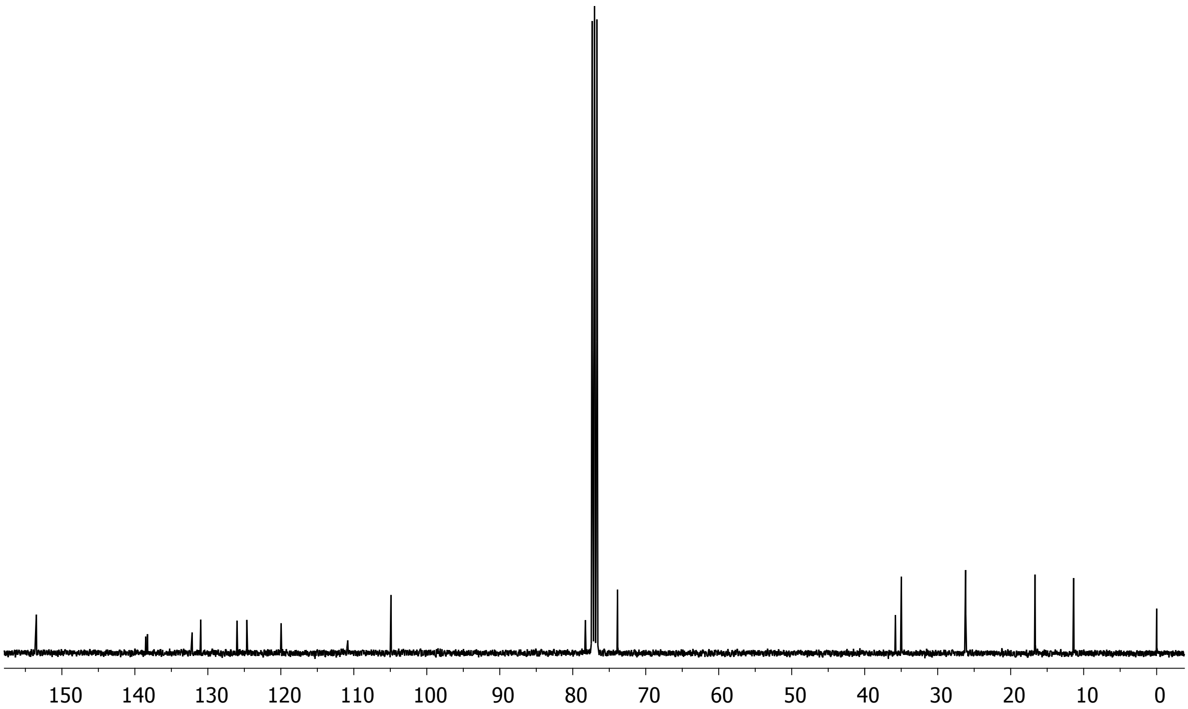
6R



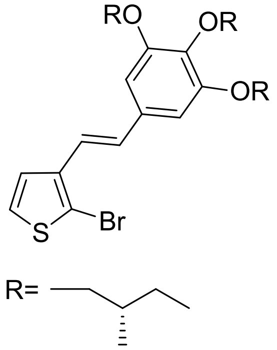
RO
OR
OR
S
Br
R=

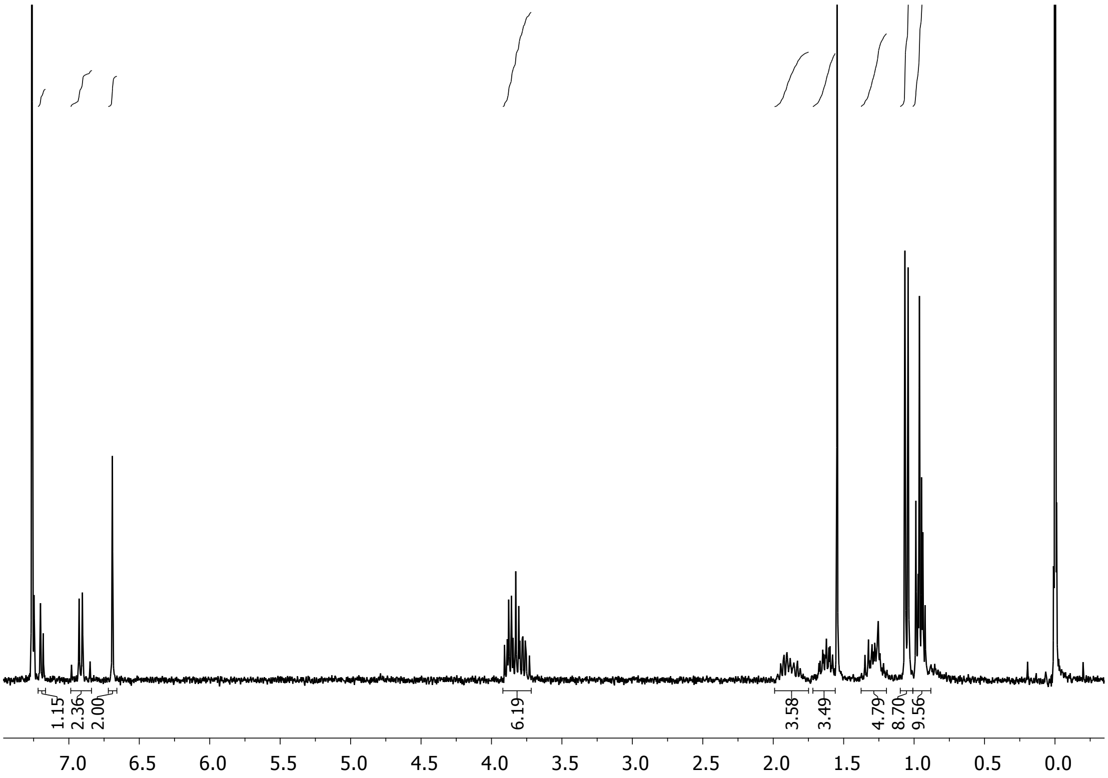


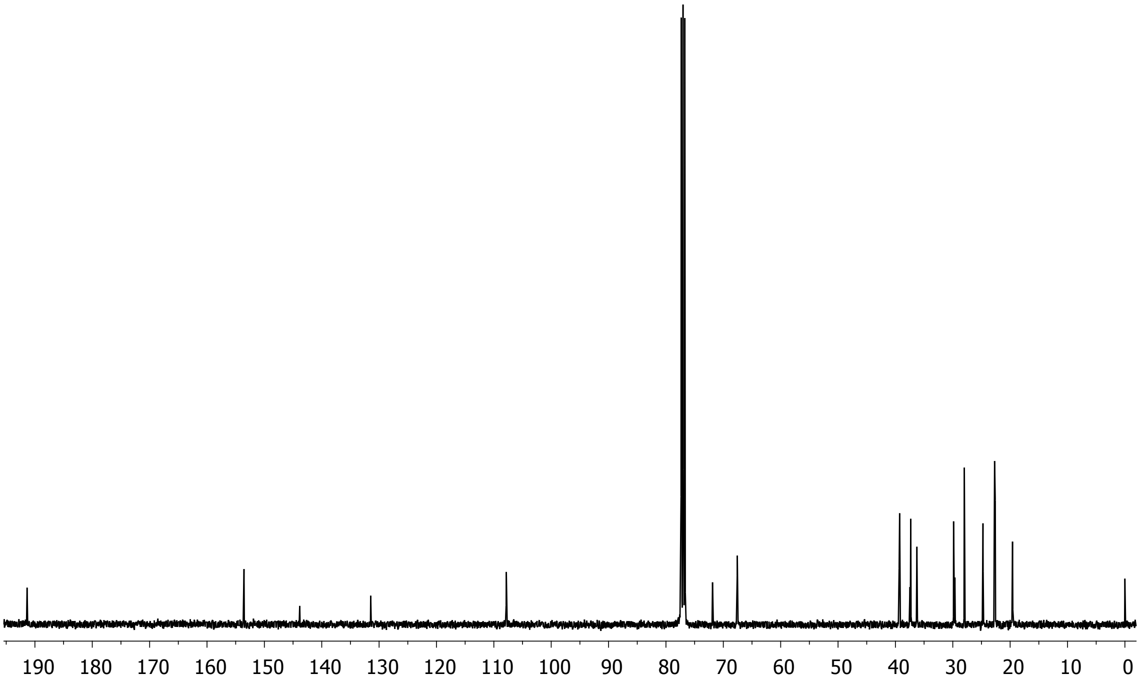
1.05
2.30
2.00
6.23
3.38
3.09
12.50
10.15
9.35
27.56
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



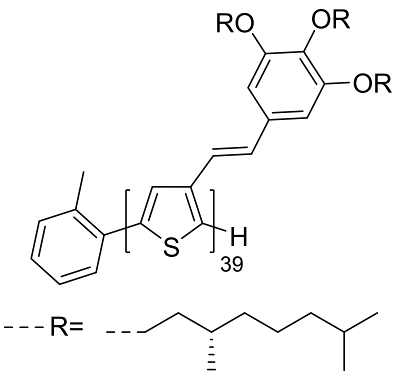
6B

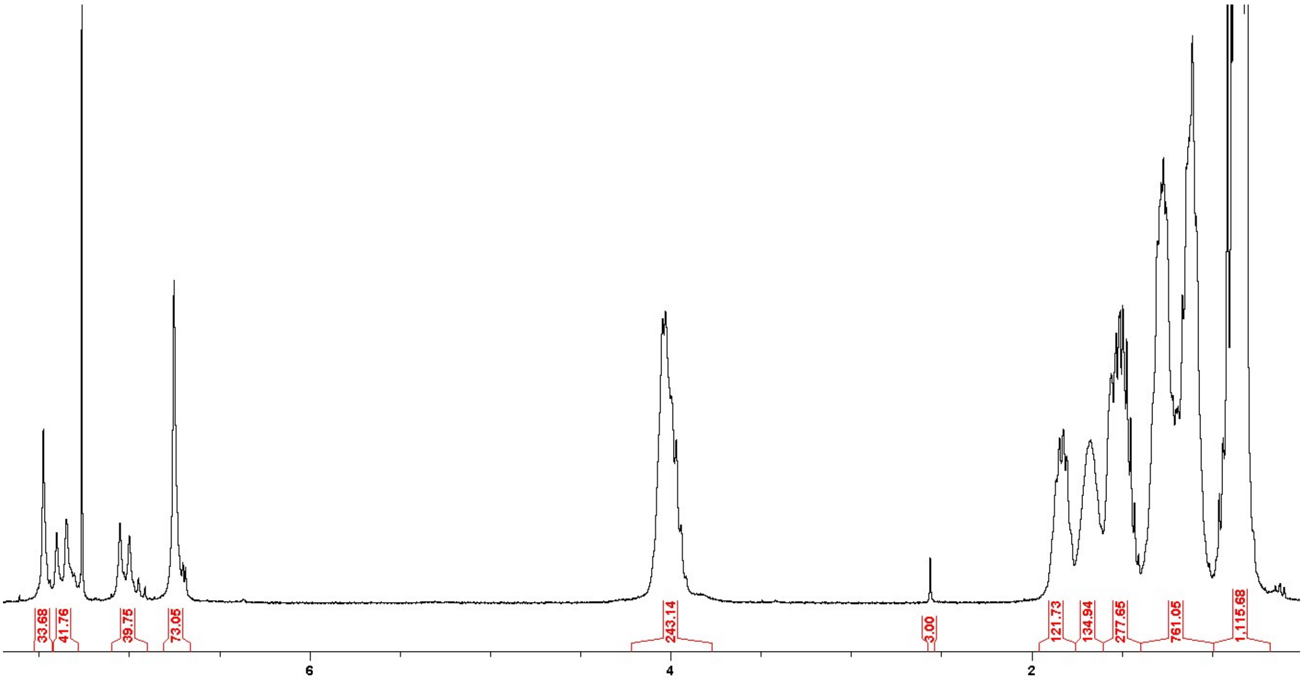



1.15
2.36
2.00
6.19
3.58
3.49
4.79
8.70
9.56
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

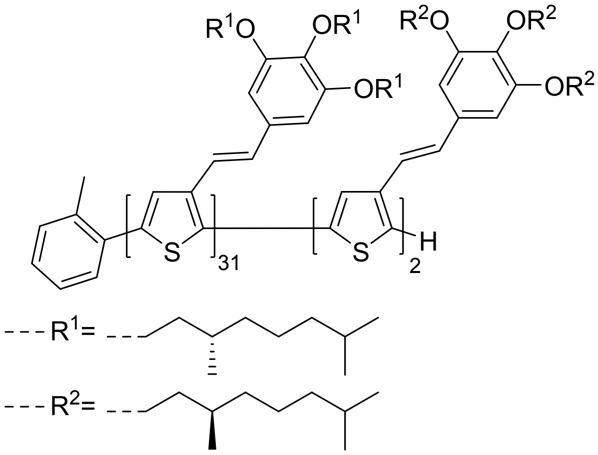
P1

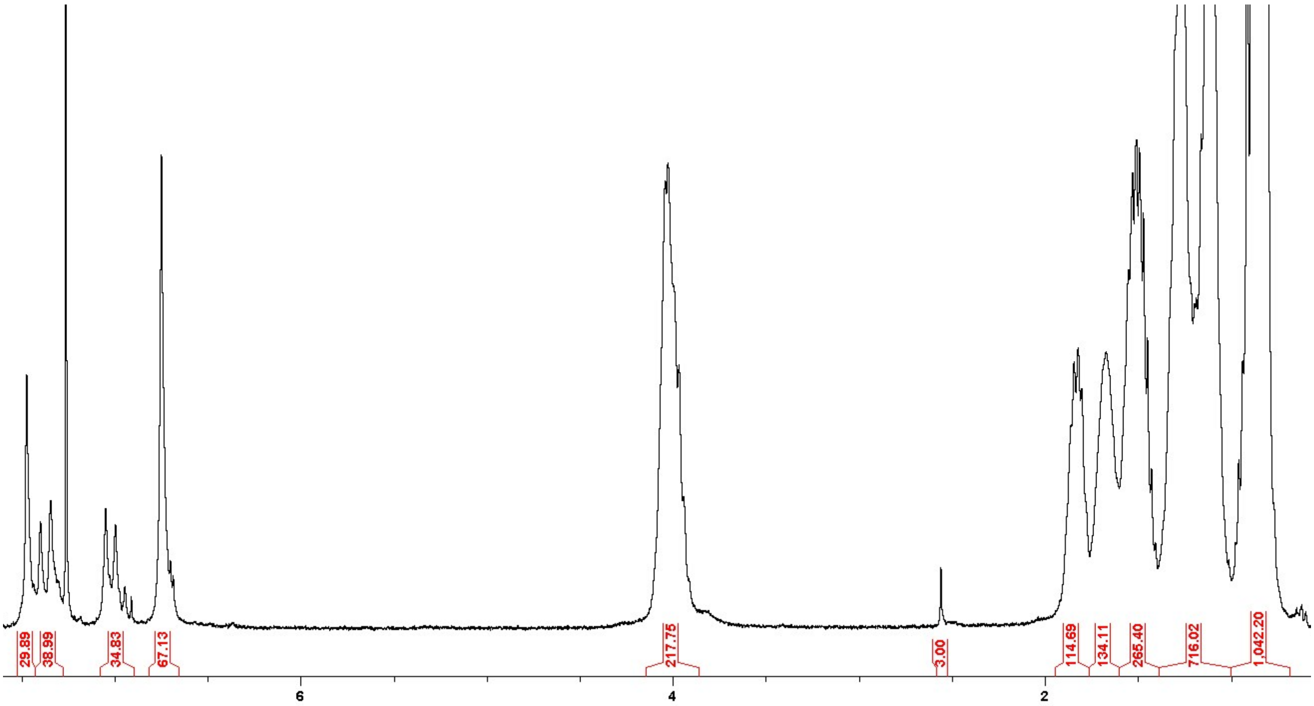




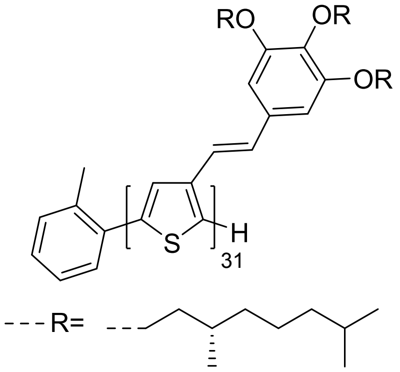
P2

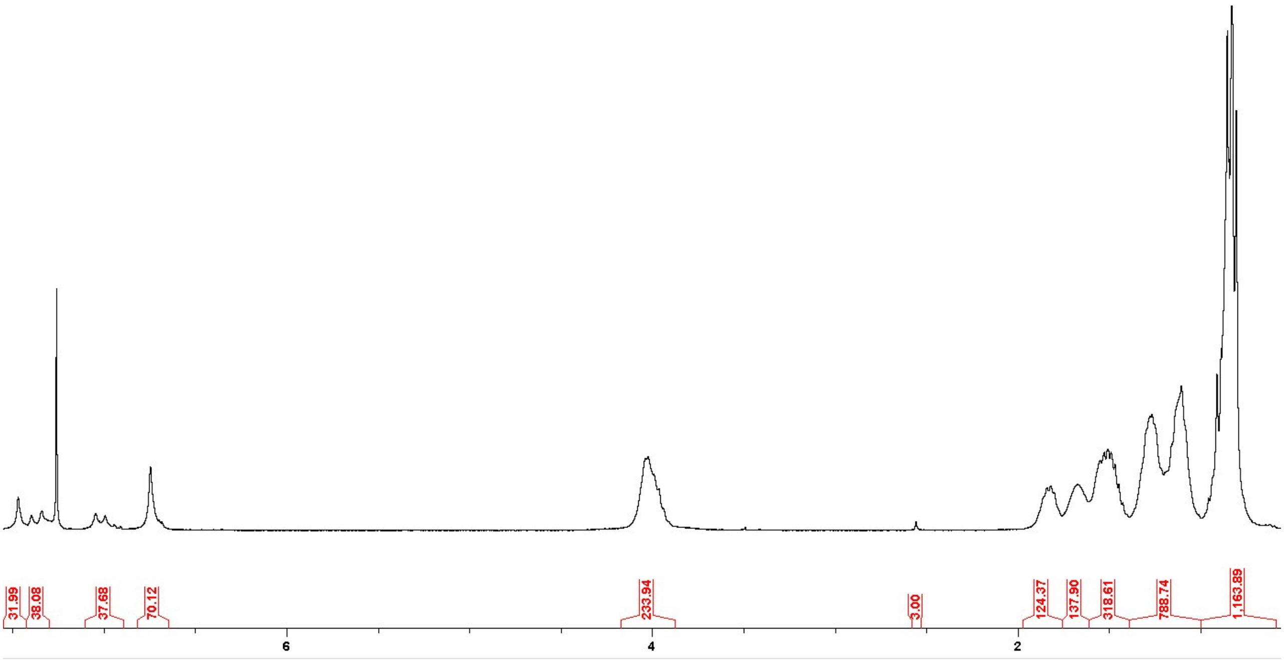
Total Block copolymer




29.89
38.99
34.83
67.13
217.75
3.00
114.69
134.11
265.40
716.02
1,042.20
6
4
2

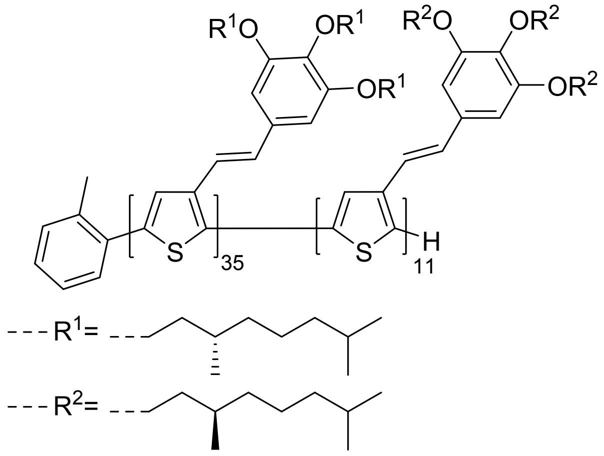
First block

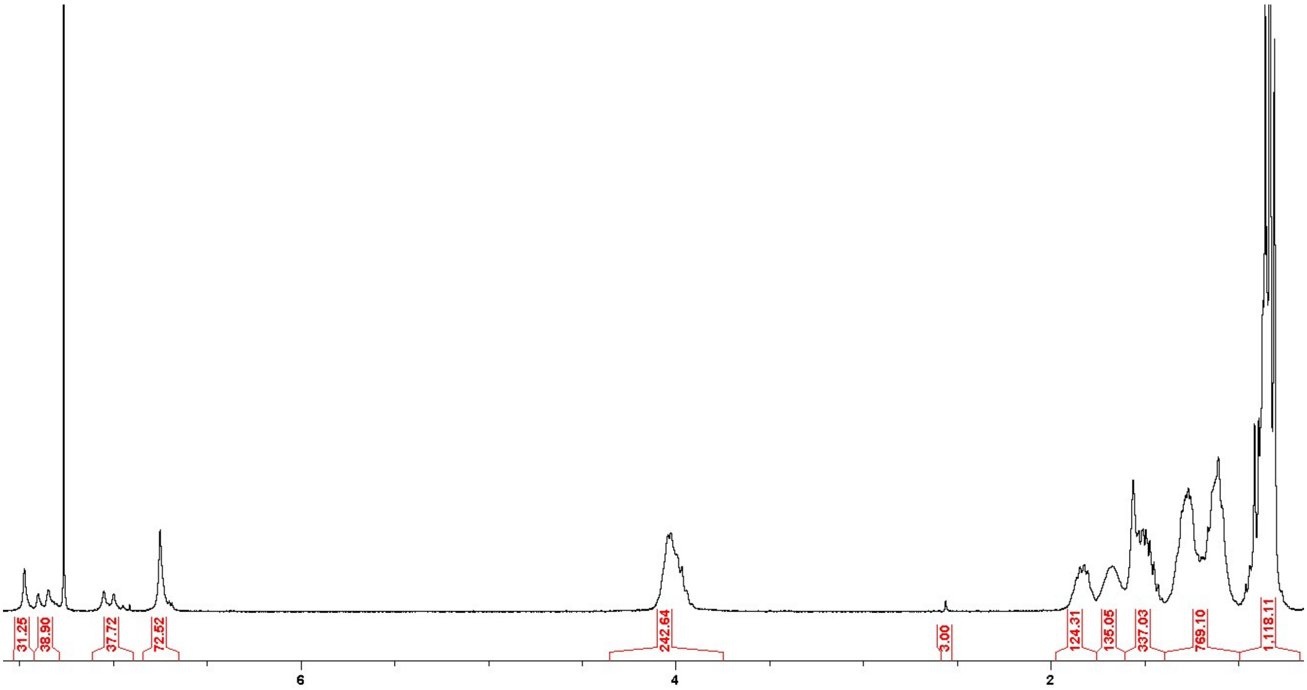

RO
OR
OR
S
H
31
R=


31.99
38.08
37.68
70.12
233.94
3.00
124.37
137.90
318.61
788.74
1,163.89
6
4
2

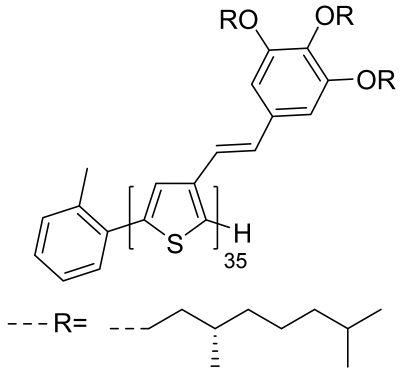
P3

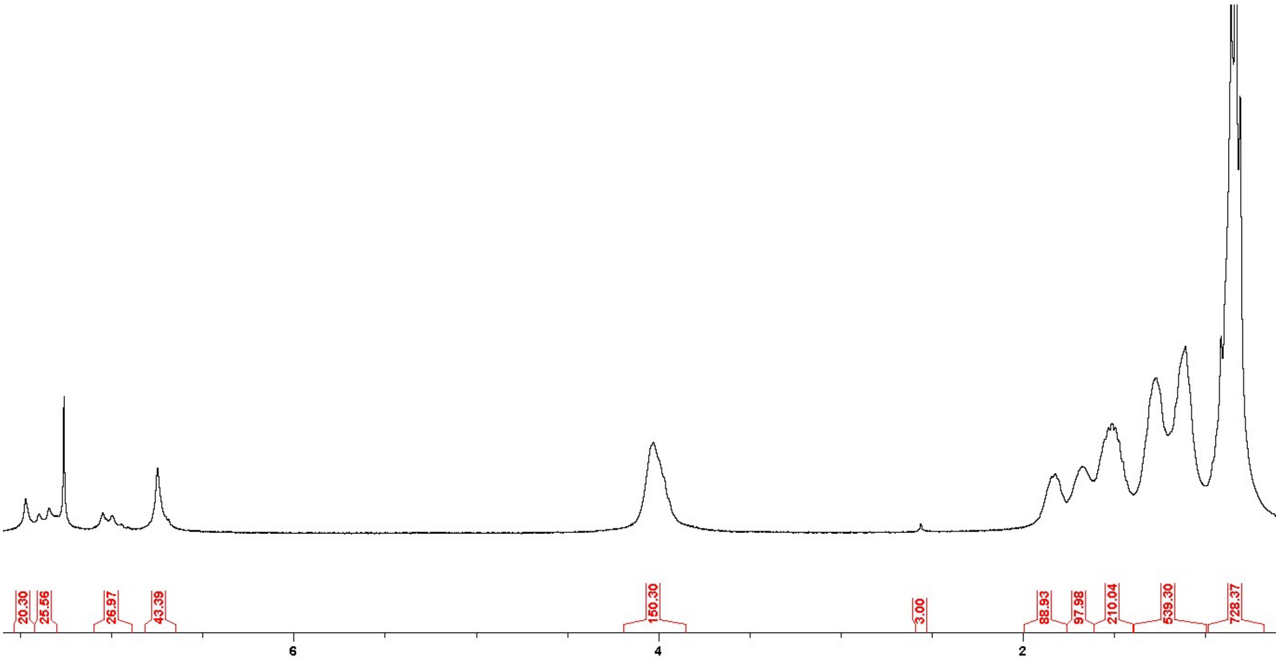
Total block copolymer





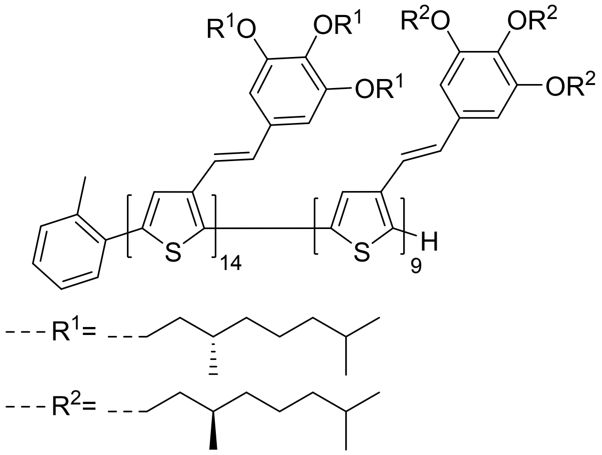
First block

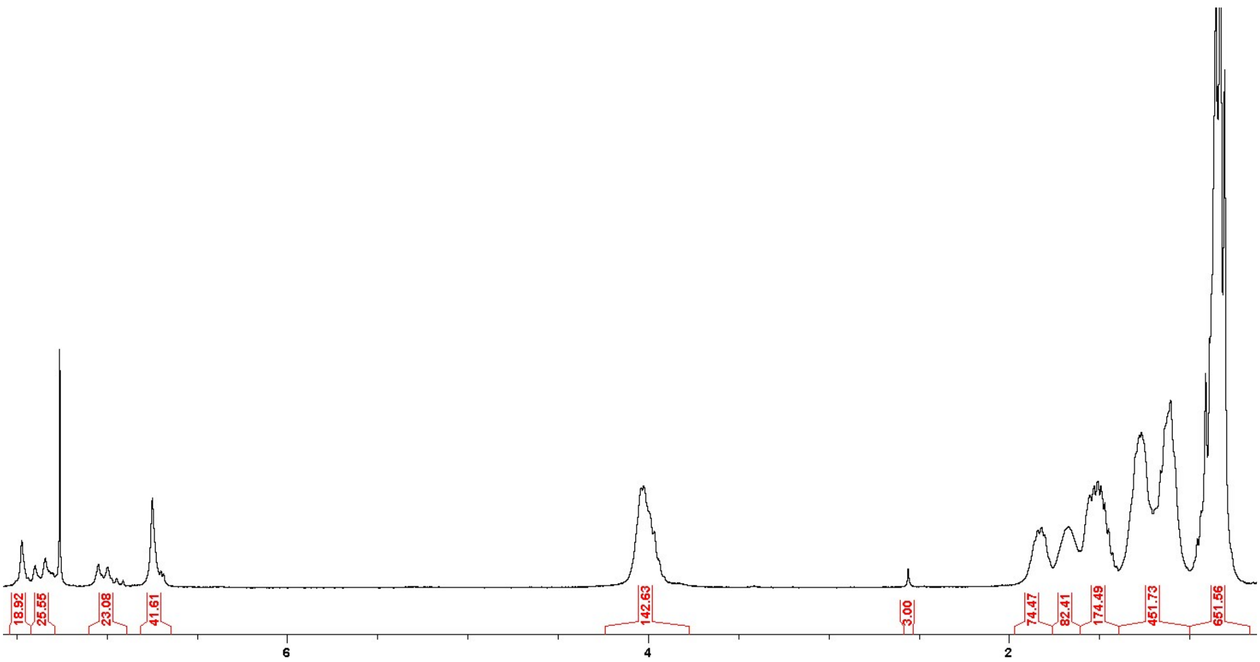




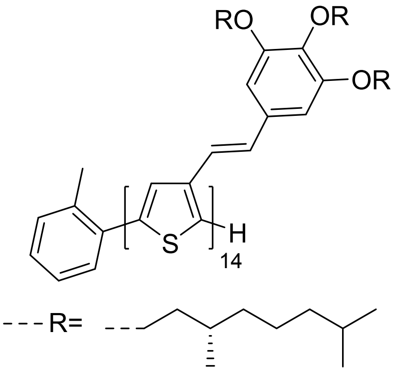
P4

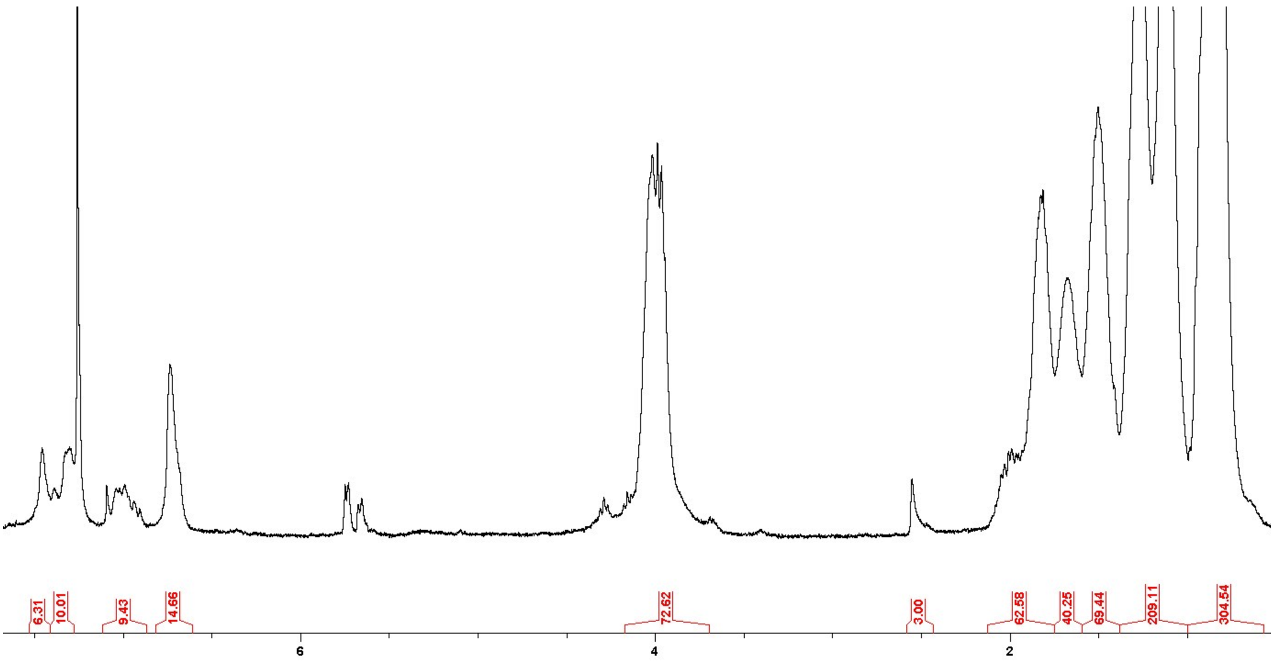
Total block copolymer




18.92
25.55
23.08
41.61
142.63
3.00
74.47
82.41
174.49
451.73
651.56
6
4
2

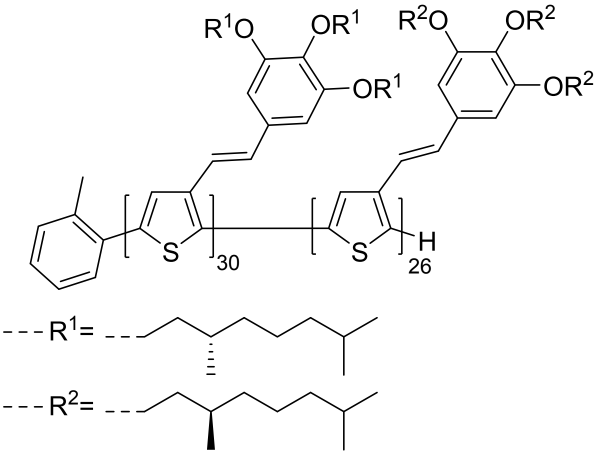
First block

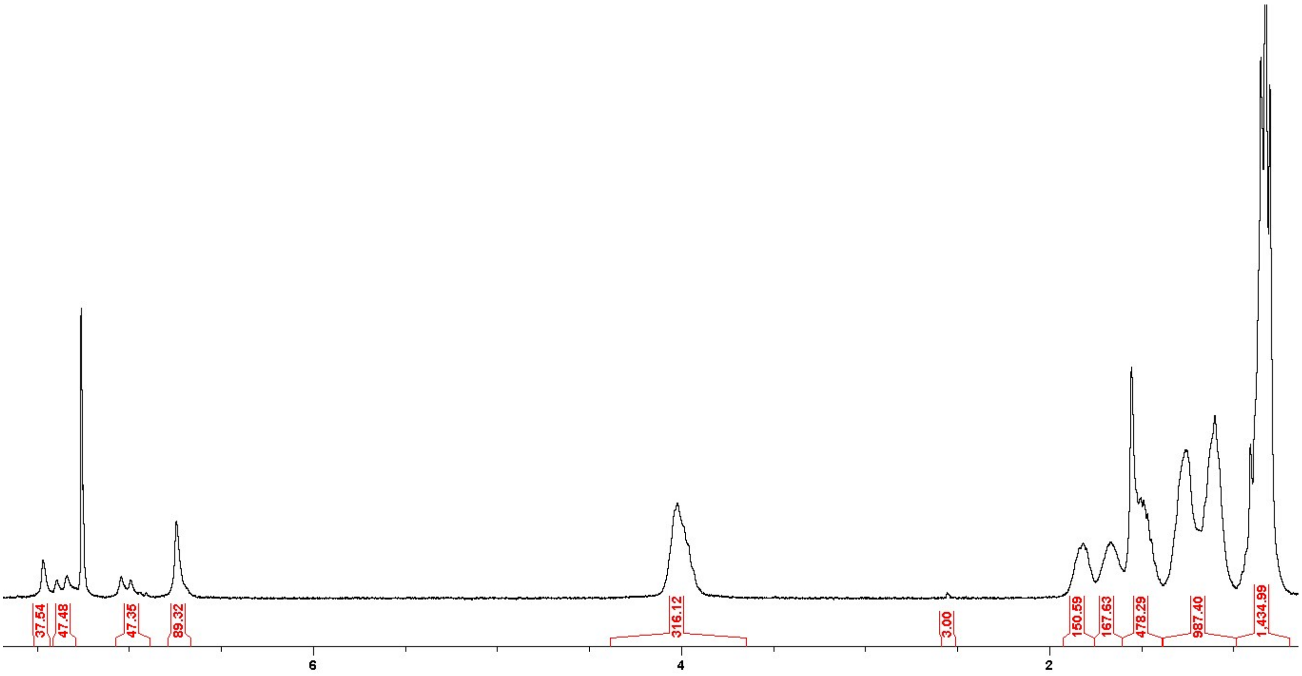

RO
OR
OR
S
H
14
R=


6.31
10.01
9.43
14.66
72.62
3.00
62.58
40.25
69.44
209.11
304.54
6
4
2

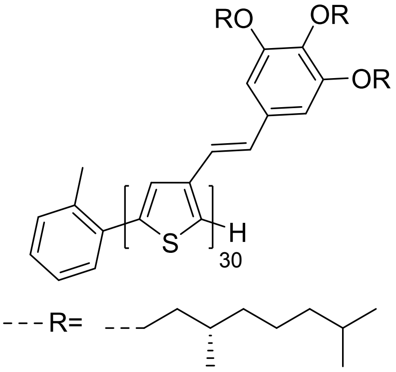
P5

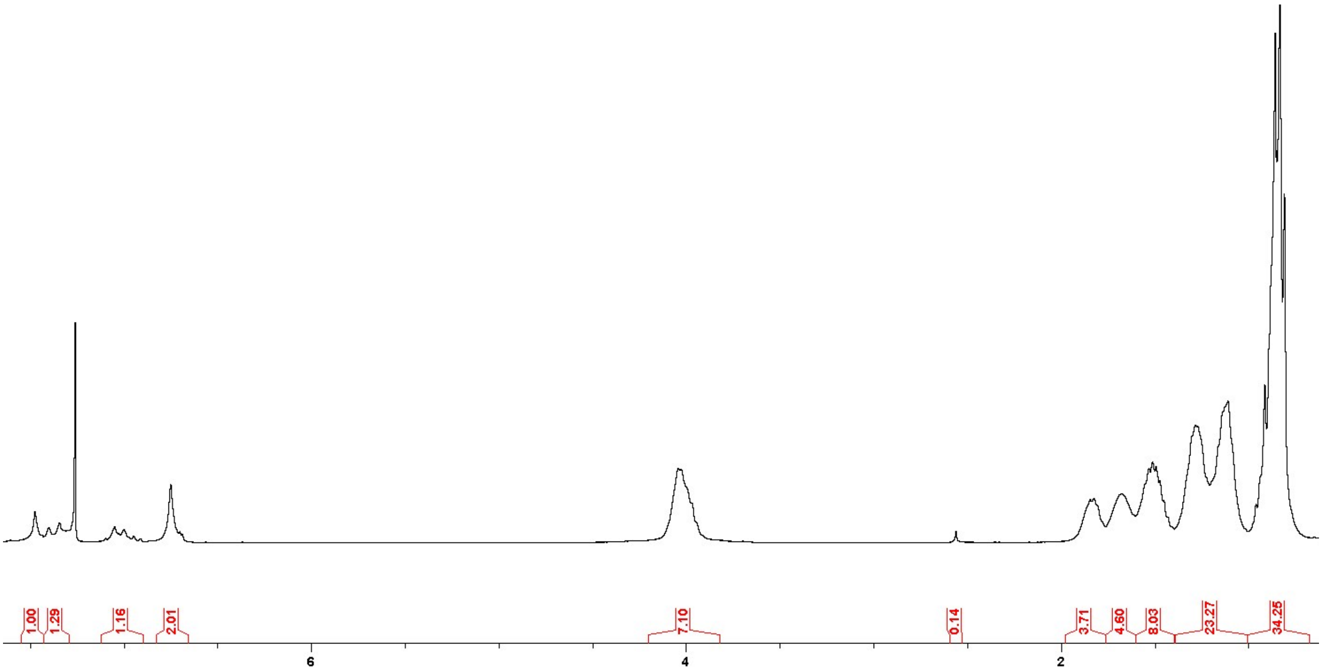
Total block copolymer





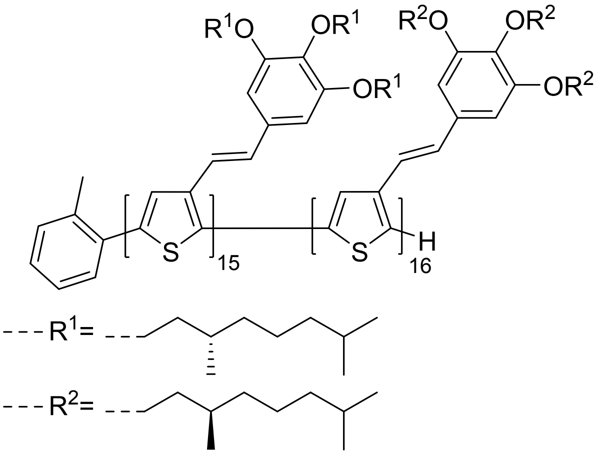
First block

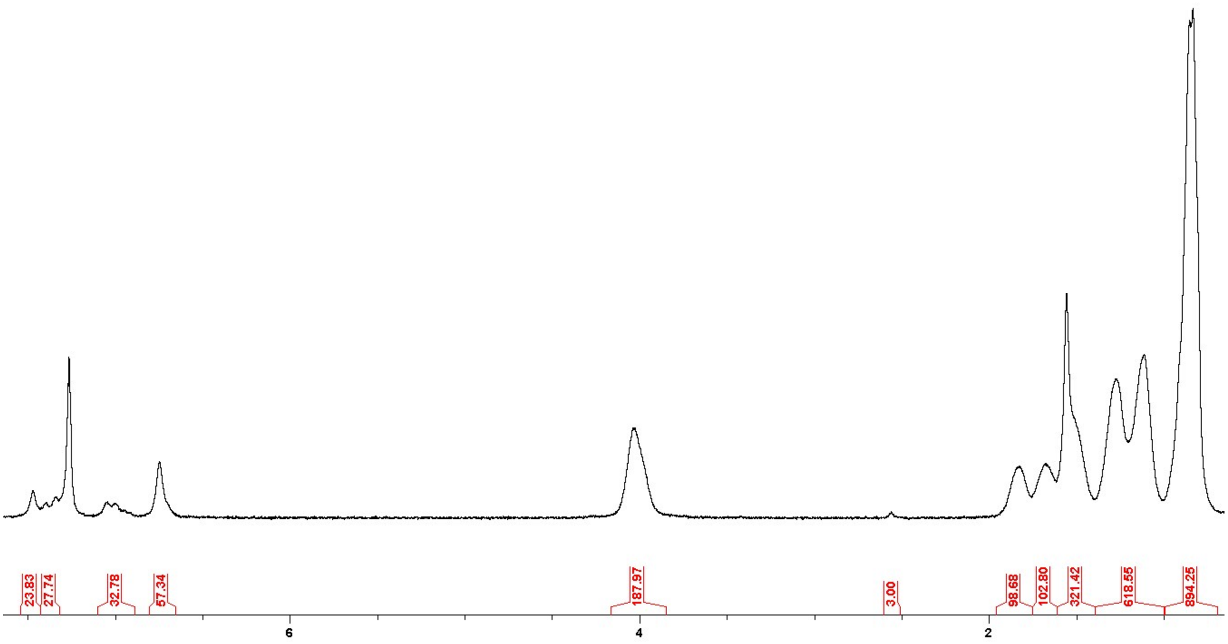




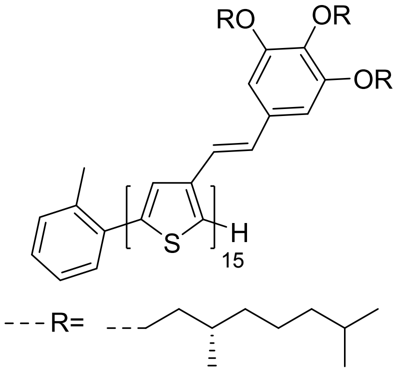
P6

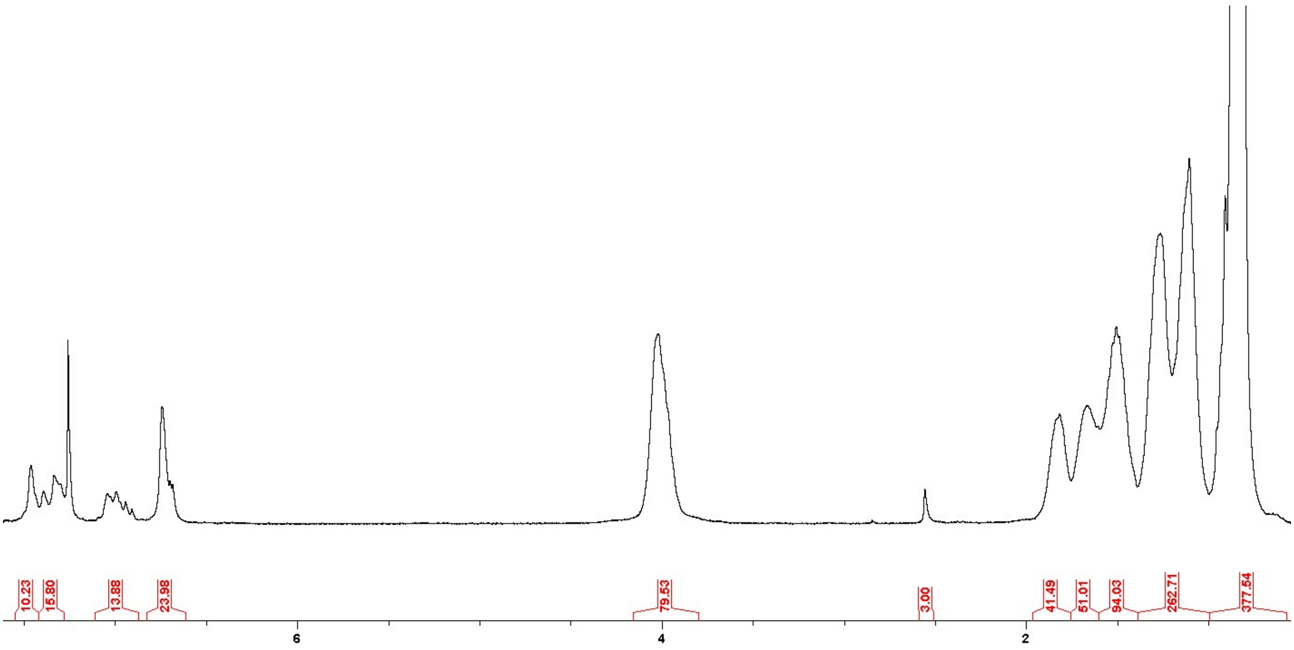
Total block copolymer



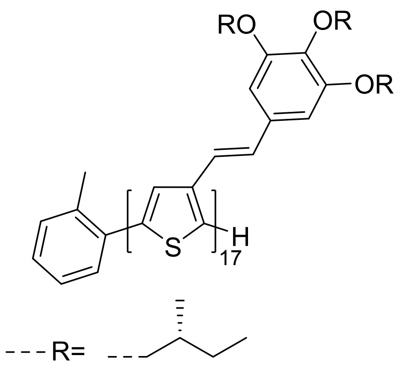

23.83
27.74
32.78
57.34
187.97
3.00
98.68
102.80
321.42
618.55
894.25
6
4
2

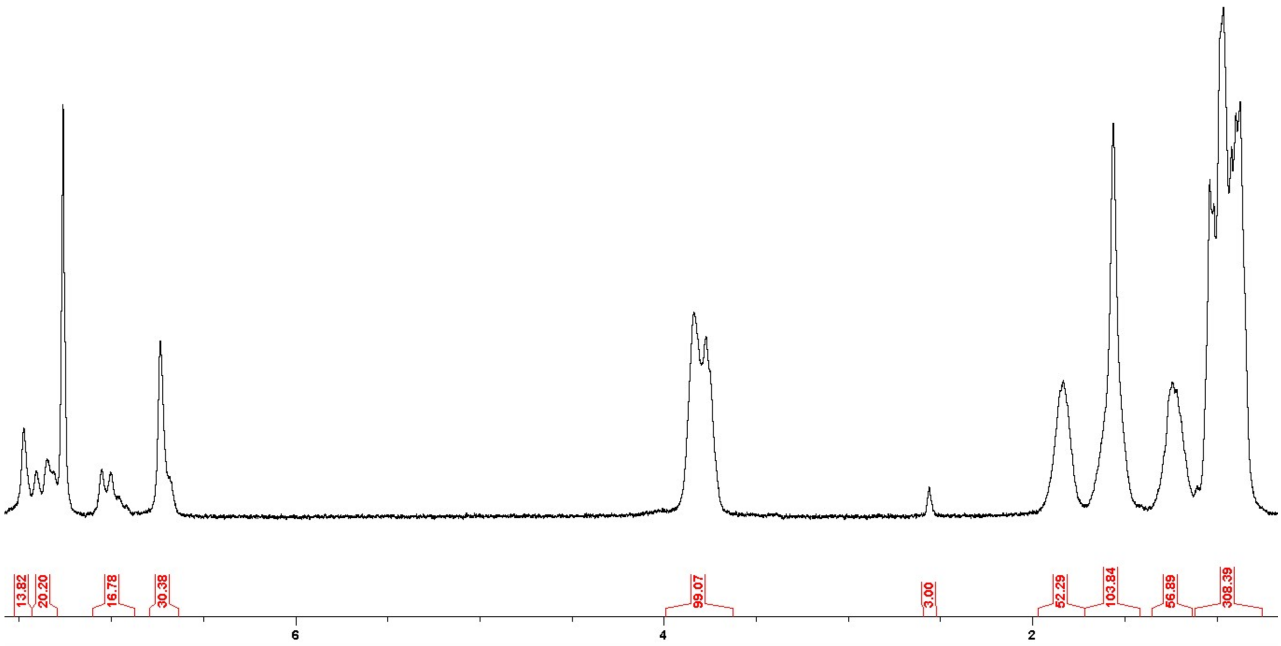
First block


RO
OR
OR
S
H
15
R=

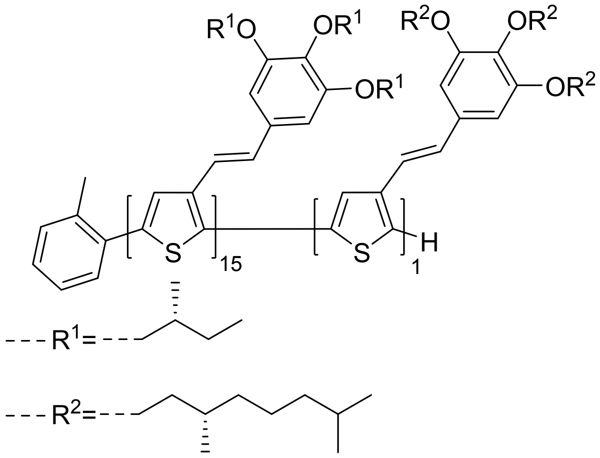

10.23
15.80
13.88
23.98
79.53
3.00
41.49
51.01
94.03
262.71
377.54
6
4
2

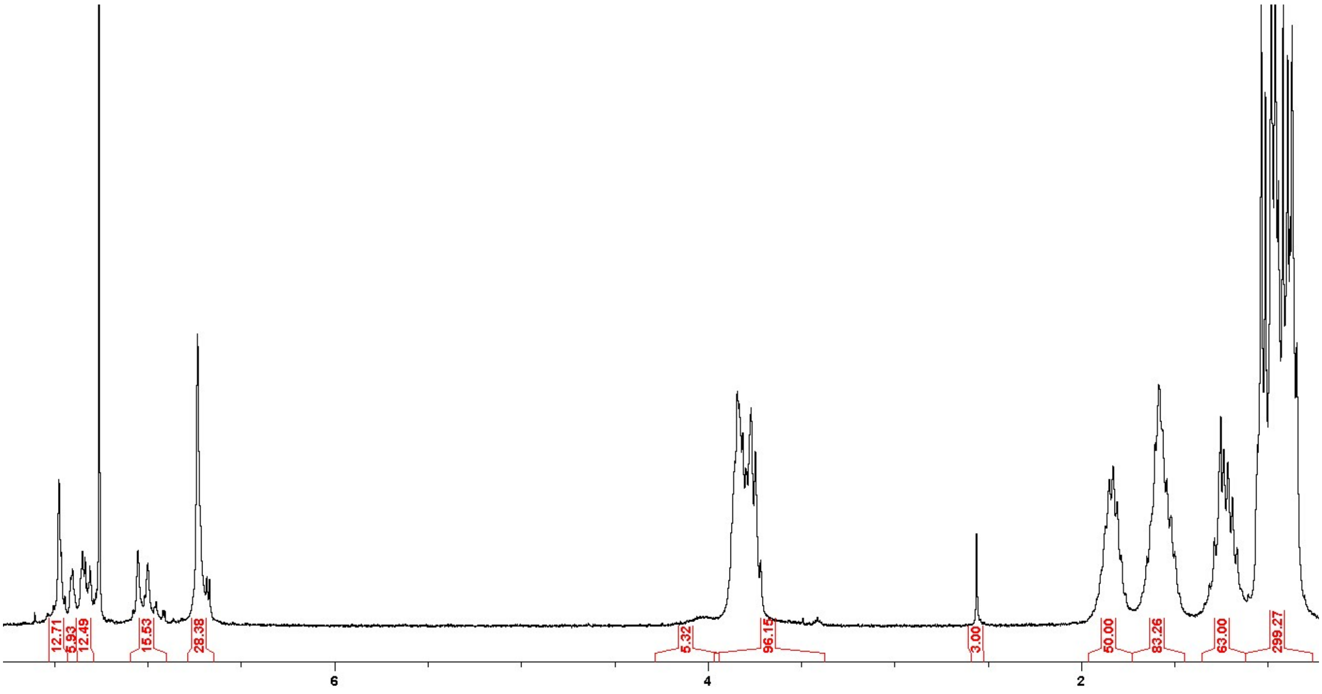
P7


RO
OR
OR
S
H
17
R=

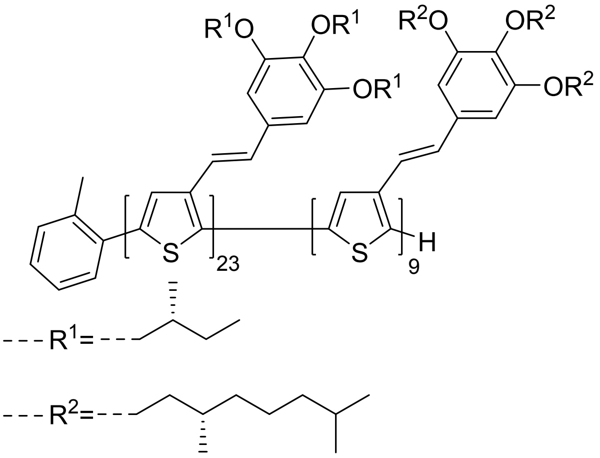

13.82
20.20
16.78
30.38
99.07
3.00
52.29
103.84
56.89
308.39
6
4
2

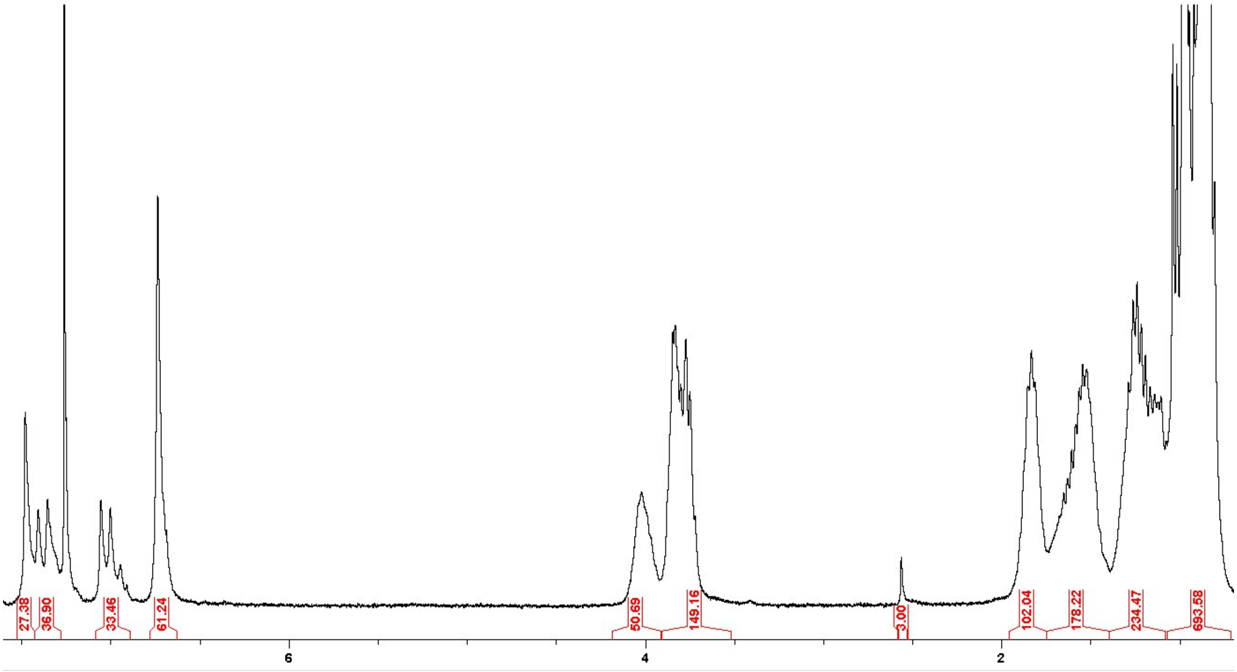
P8


R1O
OR1
OR1
R2O
OR2
OR2
S
15
S
H
1
R1=
R2=

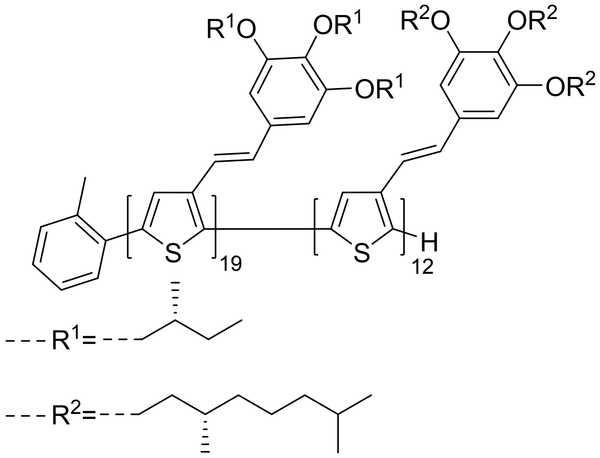

12.71
5.93
12.49
15.53
28.38
5.32
96.15
3.00
50.00
83.26
63.00
299.27
6
4
2

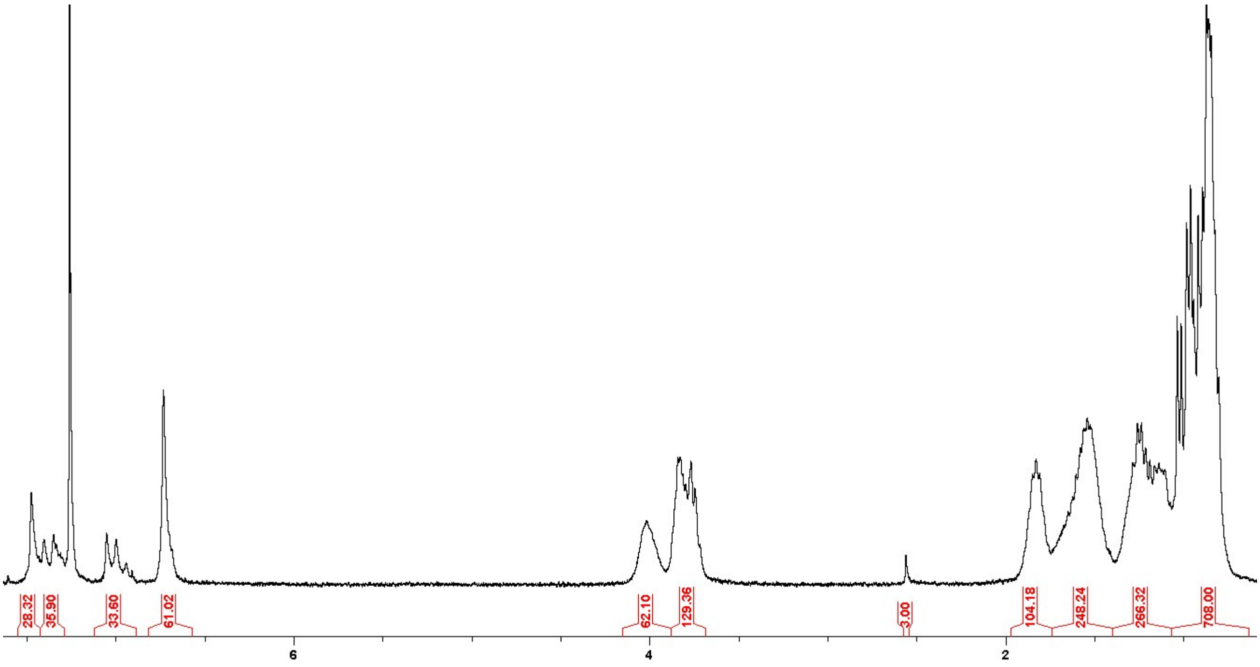
P9


R^{1}O
OR^1
OR^1
R^{2}O
OR^2
OR^2
S
23
S
9
H
R^1=
R^2=

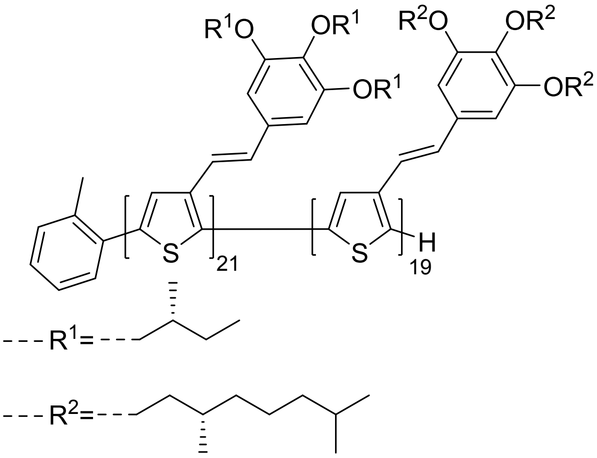

27.38
36.90
33.46
61.24
50.69
149.16
3.00
102.04
178.22
234.47
693.58
6
4
2

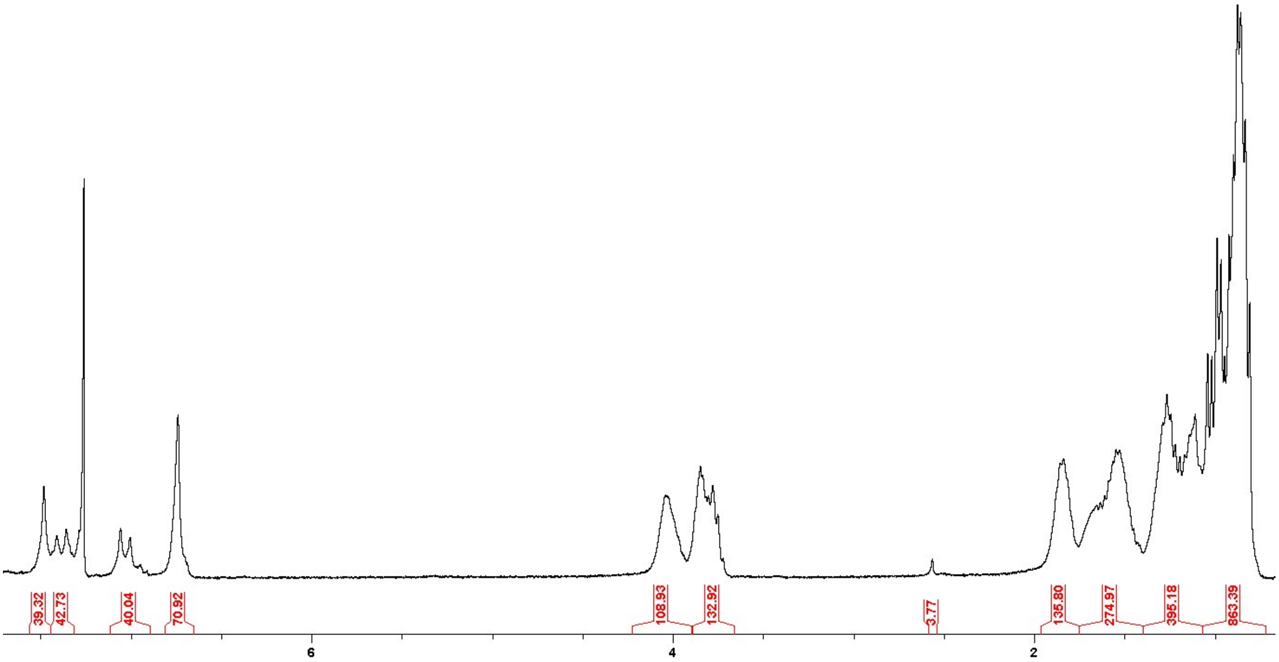
P10


R1O
OR1
OR1
R2O
OR2
OR2
S
19
S
12
H
R1=
R2=

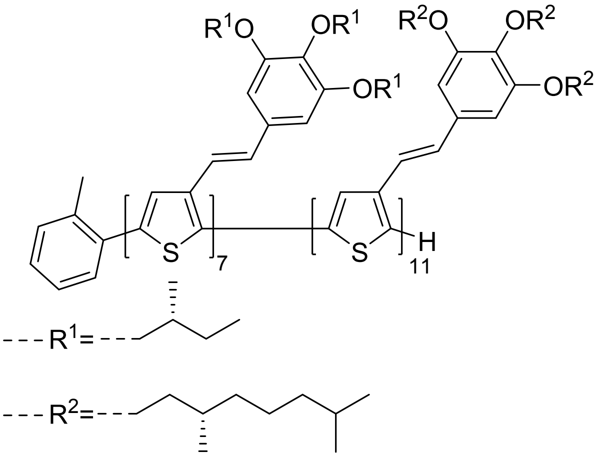

28.32
35.90
33.60
61.02
62.10
129.36
3.00
104.18
248.24
266.32
708.00
6
4
2

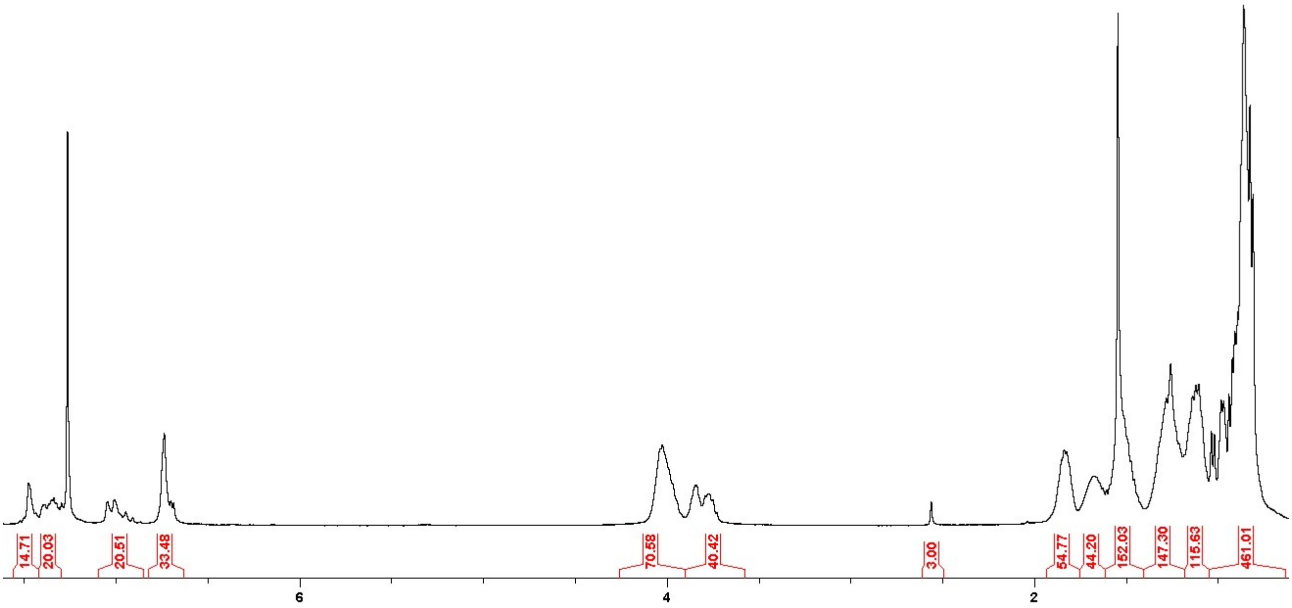
P11


R1O
OR1
OR1
R2O
OR2
OR2
S
21
S
19
H
R1=
R2=

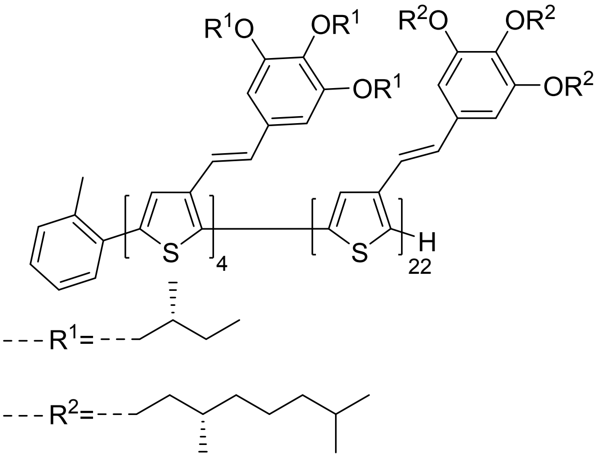

39.32
42.73
40.04
70.92
108.93
132.92
3.77
135.80
274.97
395.18
863.39
6
4
2

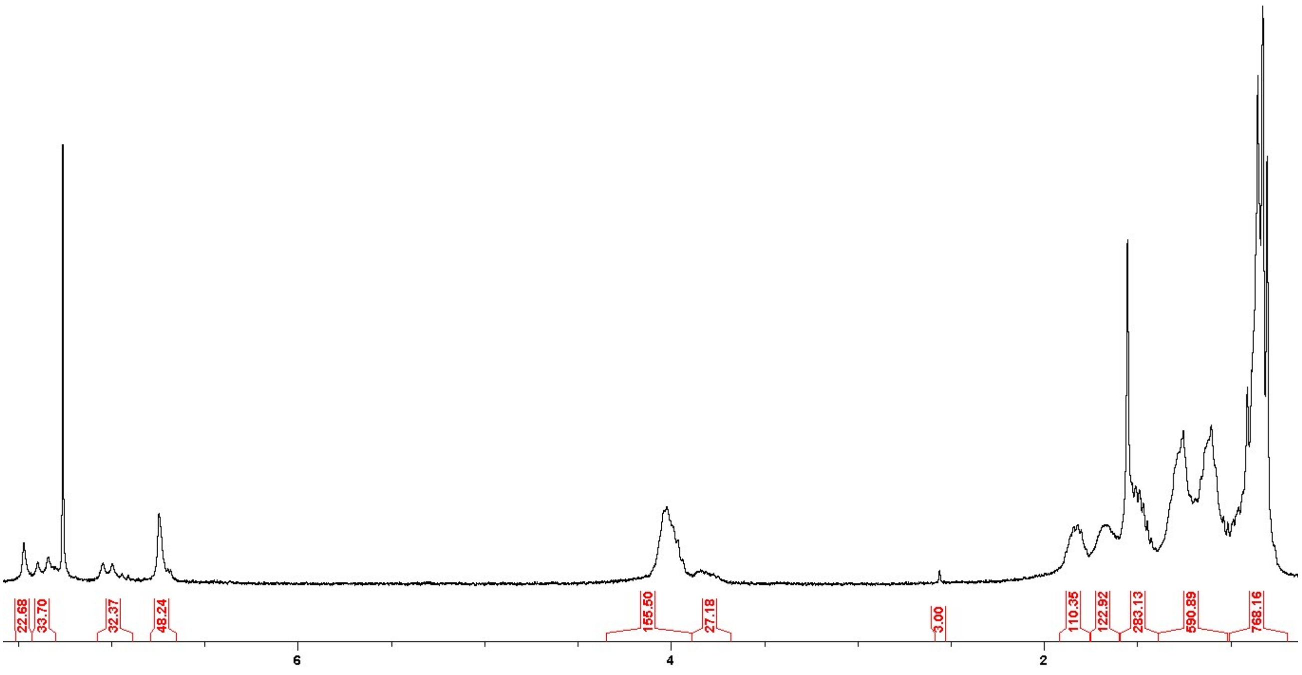
P12


R1O
OR1
OR1
R2O
OR2
OR2
S
7
S
11
H
R1=
R2=

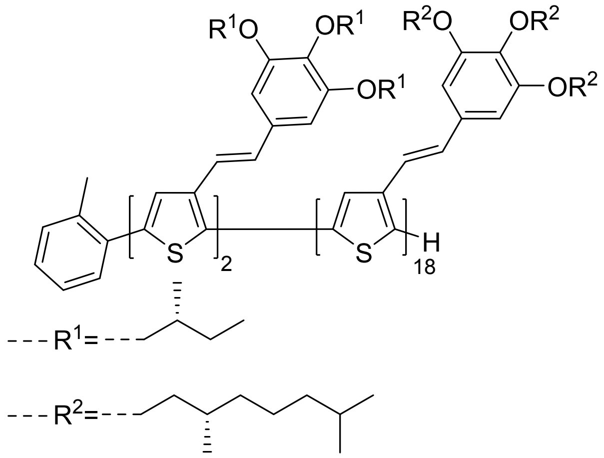

14.71
20.03
20.51
33.48
70.58
40.42
3.00
54.77
44.20
152.03
147.30
115.63
461.01
6
4
2

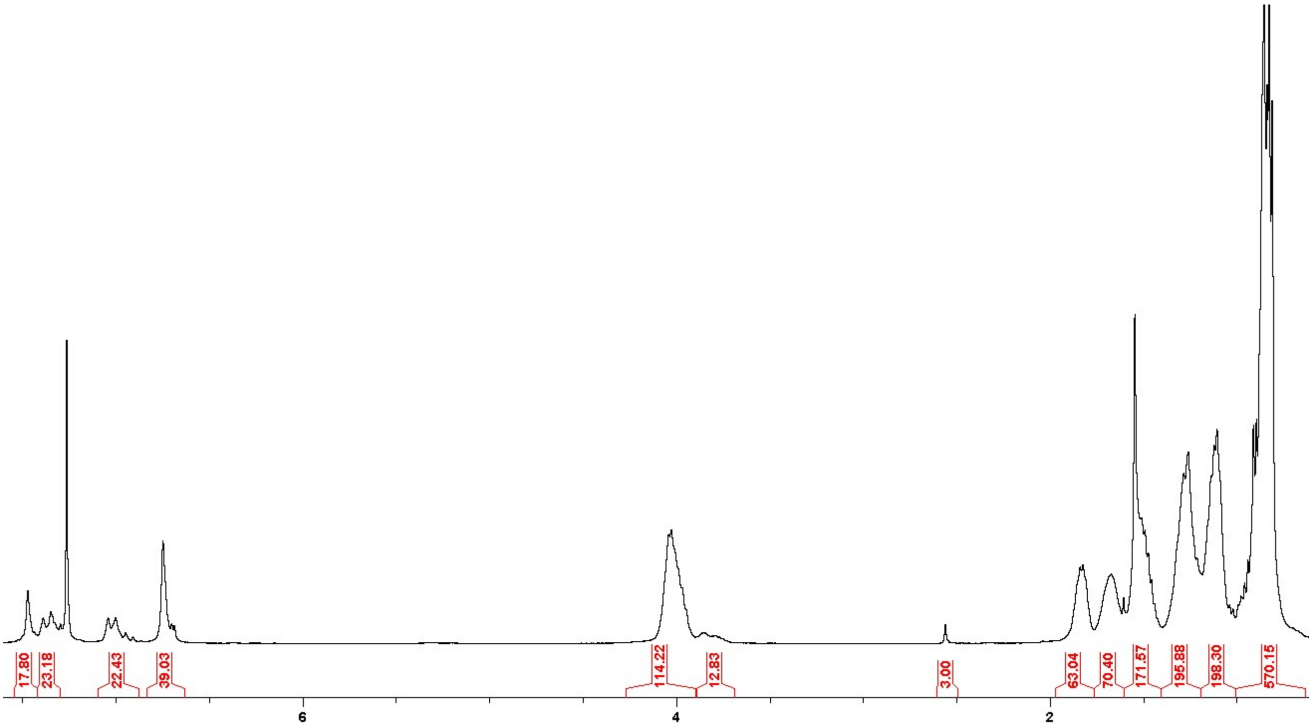
P13


R1O
OR1
OR1
R2O
OR2
OR2
S
4
S
22
H
R1=
R2=


22.68
33.70
32.37
48.24
155.50
27.18
3.00
110.35
122.92
283.13
590.89
768.16
6
4
2

P14


R^{1}O
OR^1
OR^1
R^{2}O
OR^2
OR^2
S
2
S
H
18
R^1=
R^2=



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